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Photoelectron spectroscopy of $(CO_2)_n^-$ clusters with $2 \leqslant n \leqslant 13$: Cluster size dependence of the core molecular ion

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Photoelectron spectra of the negatively charged clusters of CO_2 are recorded with 3.49 eV photon energy and appear as bell-shaped, unresolved vibrational envelopes similar to that observed for the monomer ion. The maxima of the photoelectron spectra, found by fitting the envelopes to Gaussian profiles, correspond to the vertical electron detachment energies (VDE) of the clusters. These VDE values, when combined with the previously measured value for CO_2^-, display sharp discontinuities at cluster sizes $n = 2$ and $n = 6$. The magnitudes of these shifts are on the order of 1 eV and are in near quantitative agreement with the calculated difference in VDE between the monomer anion and the D_{2d} form of the dimer anion. We infer from this agreement that the dimer ion is the core of clusters $2 \leqslant n \leqslant 5$ while the monomer ion forms the core for $n \geqslant 7$. The hexamer is special in that both forms are evident in the photoelectron spectra. These structural changes are *not* manifested as "magic numbers" in the parent spectra, which have been previously observed at $n = 4, 7, 10,$ and 14.

I. INTRODUCTION

Since the pioneering work of Klots and Compton[1] in 1977, it is now well established that homogeneous negative cluster ions of carbon dioxide, $(CO_2)_n^-$, are readily prepared by low energy electron attachment onto $(CO_2)_n$ neutral clusters formed in a supersonic expansion.[2-6] Recently, these $(CO_2)_n^-$ clusters have attracted renewed interest because pronounced intensity anomalies or magic numbers are found in negative cluster ion mass spectra under widely varying conditions.[3,5,6] It is now apparent, at least for van der Waals clusters, that these magic numbers are generally a property of the *ionic* clusters and arise as a consequence of the dynamics following ion formation.[7-11] In the $(CO_2)_n^-$ system, discontinuities in negative cluster ion intensity appear[6] at $n = 4, 7, 10, 14,$ and 16, while the cation cluster spectrum is smooth throughout this region.[12] Lineberger and co-workers[6] recently demonstrated that the negative ion discontinuities are also found in the photofragmentation patterns of mass selected $(CO_2)_n^-$ ions, proving that they are indeed associated solely with ionic behavior.

Our initial objective in this study was to obtain photoelectron spectra of mass selected $(CO_2)_n^-$ clusters to ascertain the cause of the local cluster ion stabilities evidenced in mass spectroscopy. Naively, we might have expected an exceptionally stable anion to have a higher electron affinity than its neighboring clusters and therefore display a shift in its photoelectron spectrum on the order of the stabilization energy. A moment's reflection, however, reveals that the actual situation must be more complex since photoelectron spectroscopy probes the energy *and* shape differences between the potential energy surfaces of the ion and corresponding neutral species. While the neutral surface is well approximated by a collection of loosely bound CO_2 monomers,[13] the structure of the anion cluster is not obvious. In fact, a central issue regarding the nature of $(CO_2)_n^-$ clusters

is whether the anion is formed with a delocalized electron or whether the extra electron is captured on a well defined molecular ion within an essentially neutral cluster. The former case is associated with small geometry changes upon photodetachment so that PES will yield the adiabatic electron affinity; however, spectra of a molecular ion embedded inside a large neutral cluster will depend on both the structure of the molecular ion and the extent of its solvation.

Tsukada *et al.*[14] have analyzed data from low energy electron attachment onto CO_2 neutral clusters and conclude that while the delocalized or "extended affinity" electron states are important in the electron capture process, the cluster quickly stabilizes to a state where the electron is *localized* on a few molecular centers, probably on the monomer or dimer. The stabilization energy is then released, causing evaporation of monomers which ultimately leads to anomalies in ion intensities depending on the subsequent unimolecular decomposition kinetics, as discussed by Klots[9] and recently observed by Märk and Scheier.[11]

While the localization of the extra electron on "a few molecular centers" plays a central role in the theory of $(CO_2)_n^-$ cluster ion formation, there is very little direct evidence for these core molecular ions in any negative cluster ion system. This is in contrast to the situation for positive ion clusters where the characteristic photodestruction spectrum of the $(CO_2)_2^+$ dimer was found nearly intact in larger $(CO_2)_n^+$ clusters, identifying the dimer as the core species.[12] Interestingly, Lineberger and co-workers[6] were able to extract useful information from their mass selected $(CO_2)_n^-$ photofragmentation experiments despite the fact that the nature of the UV absorption leading to fragmentation remains unknown. No characteristic chromophores have yet been determined for the $(CO_2)_n^-$ clusters. The $(CO_2)_n^-$ monomer is not stable as an isolated species,[15] and several structures have been suggested for the dimer.[16] Neither CO_2 nor its negative ion possess an excited electronic state accessible in the near UV, although pulse radiolysis studies[17] indicate

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that $(CO_2)_2^-$ has an absorption which peaks near 250 nm in aqueous solution.

Bowen and co-workers[18] have recently shed considerable light on the anion structures by obtaining photoelectron spectra of CO_2^- and $(CO_2)_2^-$ at 2.54 eV. These authors find that the dimer photoelectron spectrum is shifted so far from that of the monomer (> 1.0 eV) that only the tail of the band was observable at the 2.54 eV photon energy. This was surprising in light of the behavior of the isoelectronic series $(N_2O)_n^-$, where the monomer–dimer shift[19] of 190 meV is on the order expected for ion–molecule stabilization energies.[20] In 1987, Fleischman and Jordan reported[21] *ab initio* calculations indicating that the anomalous shift in CO_2 arises from a D_{2d} oxalate-like symmetrical form of the dimer.

In this paper, we report $(CO_2)_n^-$, $2 \leqslant n \leqslant 13$, photoelectron spectra obtained using 3.49 eV excitation from a pulsed Nd:YAG laser. The objectives of this work are to reveal the full shape of the dimer anion photoelectron spectrum and explore how the spectra of higher clusters evolve with increasing size, especially in the neighborhood of the magic numbers $n = 4, 7$, and 10. A primary conclusion of this work is that the huge monomer/dimer shift observed by Bowen and co-workers[18] at 2.54 eV is found to be *reversible* at larger cluster size. A rationalization of this behavior based on differential solvation of the core ion, originally suggested by Fleischman and Jordan,[21] appears consistent with this data. Interestingly, the photoelectron spectra reveal a large change in ion structure in going from $n = 5$ to $n = 6$, while the mass spectra are quite regular through this transition.

II. EXPERIMENTAL

A schematic diagram of the experimental setup is shown in Fig. 1. The apparatus consists of a pulsed cluster ion source, time-of-flight mass selector, pulsed Nd:YAG laser, and time-of-flight photoelectron energy analyzer. A detailed description of the apparatus is contained in Refs. 22 and 23, which concern its application to the $(O_2)_n^-$ and $N_2O_2^-$ systems.

Negative carbon dioxide clusters are formed by 1 keV electron impact ionization of a pulsed supersonic expansion of pure CO_2 (1 atm stagnation pressure), as described by Alexander *et al.*[6] The ionized expansion forms a dense neutral plasma in which the incident high energy electrons are scattered while the slow secondary electrons are trapped in the jet. These slow electrons are then cooled in the expansion *via* inelastic collisions and a small fraction ultimately associate onto neutrals to form negative ions. Since we have never observed the CO_2^- monomer ion under any circumstances, we infer that the $(CO_2)_n^-$ clusters are formed by dissociative electron attachment onto neutral clusters of CO_2. This suggestion is supported by the observation that the cluster size distribution for small clusters ($n < 16$) is insensitive to the distance downstream where the electron beam ionizes the jet.

The process of negative ion formation by dissociative electron attachment onto neutral clusters has been observed by several groups[1-4,15,24] who cross a neutral cluster beam with a controlled low energy electron beam. The negative ion cluster size distribution is found to be electron energy dependent[3,15,24] in such a way that the larger ($n > 4$) clusters are readily formed with near zero energy electrons, while smaller clusters such as the dimer are only produced above a threshold energy of about 1.5 eV. Apparently, the characteristic energy of the electrons in our source is lower than this threshold since the small clusters ($n < 5$) appear as very low intensity peaks in the time-of-flight mass spectrum shown in Fig. 2(a). In order to generate a dimer ion beam of sufficient intensity for this study, we found it necessary to increase the
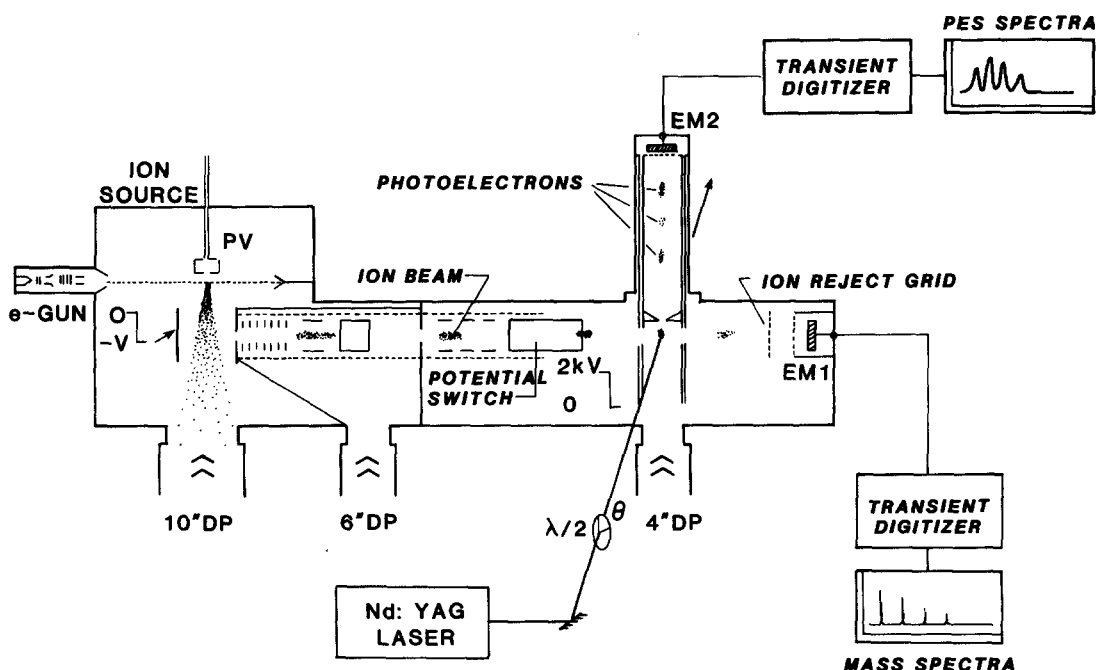

FIG. 1. Schematic diagram of experimental apparatus. EM = electron multiplier, DP = diffusion pump, $\theta = 55°$, PV = pulsed valve.
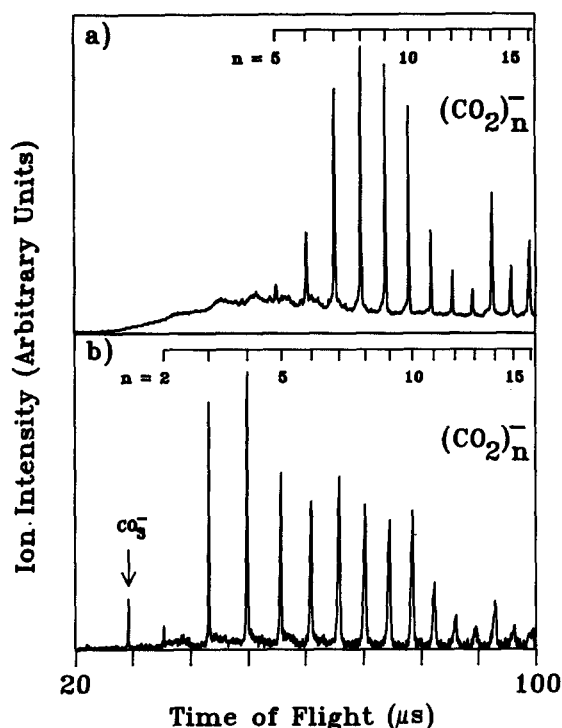
FIG. 2. Time-of-flight mass spectra of $(CO_2)_n^-$ clusters with two different voltages on the tungsten loop (see the text): (a) 0 V with respect to valve, and (b) — 60 V with respect to valve.

energy of the free electrons in the jet by applying about 60 V to a tungsten loop about 3 mm outside the nozzle. Note that this voltage does not correlate directly to electron energy in the high density part of the jet due to the shielding effect of the plasma. A typical mass spectrum taken under these conditions is shown in Fig. 2(b), where the size distribution now peaks at $n = 4$. In addition, the CO_3^- molecular ion is now evident which is known to have a formation threshold of about 3 eV.[1] In practice, the voltage on the loop, the electron beam-nozzle crossing distance, and the backing pressure are empirically varied to maximize the intensity of each cluster ion. Some caution must be exercised in interpreting the formation mechanism from these mass spectra since, except for the presence of CO_3^-, the small cluster distribution in Fig. 2(b) is almost identical to that found by Stamatovic et al.[3] who used near zero energy electrons and a 5 bar expansion with a nozzle cooled to — 20 °C.

Photoelectron spectra were recorded with the electric vector of the laser oriented at 55° (the magic angle) with respect to the electron flight tube. We have also carried out a few scattered determinations of the angular anisotropy of the ejected electron and find that the distribution is strongly skewed along the electric vector. The resolution of this time-of-flight spectrometer is dependent on the electron energy and varies from about 35 meV at one electron volt to 150 meV at two electron volts. Photoelectrons with center-of-mass energy ($E_{c.m.}$) smaller than 0.35 eV are not reproducibly collected and are therefore not presented. Data analysis was performed only on electrons with $E_{c.m.}$ greater than 0.50 eV. Spectra are plotted as electron binding energy E_b defined as $E_b = h\nu - E_{c.m.}$. Photoelectron spectra were calibrated

using O_2^- as a standard, run both before and after $(CO_2)_n^-$ runs.

Data were collected at a repetition rate of 10 Hz and each spectrum represents an accumulation of between 10 000 and 140 000 shots. The signal-to-noise enhancement in the spectra of $n = 5$, 6, and 8 results solely from the increased number of laser shots averaged. Laser powers were in the range of 5–35 mJ/pulse and no power dependent processes were observed. Alexander et al.[6] have reported that $(CO_2)_n^-$ clusters do not efficiently photodissociate below $n = 14$ at 355 nm, hence we only report here the photoelectron spectra of $2 \leqslant n \leqslant 13$ in order to minimize sequential two photon processes such as photodissociation followed by photodetachment.[22]

III. RESULTS

A. General observations

An overview of the $(CO_2)_n^-$, $2 \leqslant n \leqslant 13$ photoelectron spectra is presented in Fig. 3. All spectra appear as partially developed, bell-shaped envelopes containing no reproducible fine structure. Except for the position of the maxima, these spectra are quite similar to that of CO_2^- obtained by Coe et al.[18] Even though the resolution of that study (≈ 30 meV) is significantly higher than that reported here over the entire spectrum, the monomer anion photoelectron spectrum still displays only poorly resolved vibrational structure superimposed on a bell-shaped envelope. The shape of the monomer spectrum results from the large geometry change
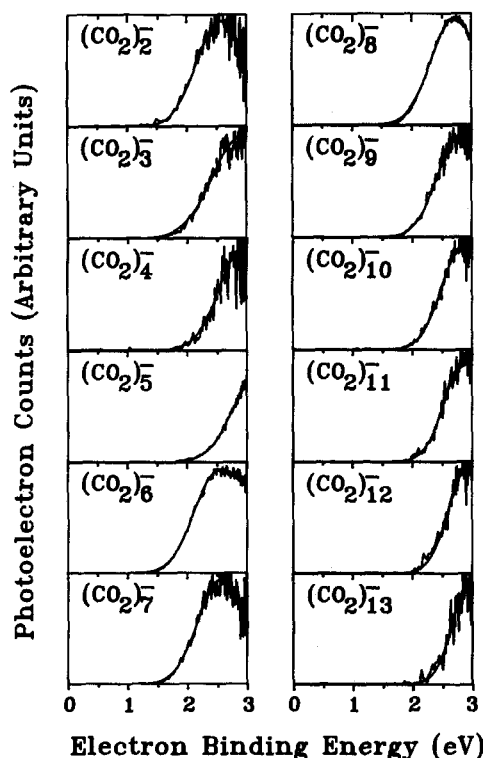

FIG. 3. 3.49 eV photoelectron spectra of $(CO_2)_n^-$ clusters for $2 \leqslant n \leqslant 13$. Spectra are plotted as electron binding energy E_b defined $E_b = h\nu - E_{c.m.}$, where $E_{c.m.}$ is the center-of-mass electron energy. Solid curves are least squares fits to a Gaussian line shape.

going from the bent anion $(\theta \approx 134°)$[15] to linear CO_2, which causes high excitation of bending vibrational modes $(h\nu_2 \approx 80 \text{ meV})$. The peak in the monomer vibrational envelope corresponds to excitation of about $25\nu_2$. We attempted to uncover traces of structure in the higher clusters at $n = 5$, 6, and 8 by carrying out long integrations; however, this averaging only served to smooth the spectra into near Gaussian envelopes. A maximum is observed in all photoelectron spectra with the exception of $n = 5$.

B. $(CO_2)_2^-$

A significant result of this study is that most of the dimer anion spectrum is observed, complementing the results of Coe et al.[18] who used 2.54 eV photons and could therefore only detect the rising edge around 2 eV detachment energy. The peak of the dimer is seen from Fig. 3 to occur at about 2.5 eV, shifted by *more than one electron volt* from the peak of the monomer at 1.4 eV.[18] On the other hand, the width of the dimer spectrum is about 1 eV FWHM, nearly the same as that of the monomer (≈ 0.9 eV).[18]

C. Higher clusters: A break between $(CO_2)_5^-$ and $(CO_2)_6^-$

At a qualitative level, the spectra from higher clusters naturally fall into two progressions: one from $n = 2$ to $n = 5$ and another from $n = 6$ to $n = 13$. The spectra from each progression are essentially identical in shape, but shifted by a few tenths of an electron volt higher in binding energy with each additional CO_2 monomer. These small shifts are on the order of magnitude expected for solvation of an ionic core. This increase in binding energy continues until $n = 6$, which shifts by about 1 eV lower in binding energy compared to $n = 5$, *opposite* to the behavior expected from solvation. Also, the spectrum of $n = 6$ is unique in that it is clearly asymmetric. The high binding energy side of the peak does not fall as quickly as $n = 7$ or $n = 8$ where the high binding energy side of the spectrum is clearly dropping off in intensity before the instrumental cut-off. The maxima of the spectra from $n = 6$ to $n = 13$ again follow a slowly changing pattern where each is consecutively higher in binding energy by about 0.1 eV. The envelope widths of the $n = 6$ to $n = 13$ sequence are a bit narrower but not qualitatively different from that of the $2 \leqslant n \leqslant 5$ sequence.

D. Analysis of the band contours

As discussed in Sec. III A, the CO_2^- monomer ion photoelectron spectrum is observed[18] to be bell shaped, as expected for a process dominated by vibrational overlap between a bent ion $(\theta \approx 134°)$[15] and linear neutral. In this case, the shape of the photoelectron *envelope* is analogous to the absorption spectrum from a vibrational ground state to a repulsive electronic state. To the extent that the absorption occurs to a relatively linear region of the upper potential curve, the absorption spectrum typically mirrors the shape of the ground state Gaussian vibrational wave function "reflected" on the tilted upper curve.[25] When the absorption is confined to a small energy region, the shape of the spectrum is also approximately Gaussian with a width determined by the Franck–Condon factors for the bound–free transition. In

this study, the photoelectron spectra are analyzed with the model that vertical transitions from bent forms of the anions occur to the bound neutral surface in a strongly repulsive region of the bending mode, giving rise to Gaussian envelopes as in photoabsorption. This procedure is motivated by theoretical predictions that the anions should be highly distorted, which are qualitatively supported by the similarity between the spectra of the monomer anion and the higher clusters. Of course, clusters with $n \geqslant 2$ are expected to have less structured envelopes than the monomer owing to excitation of intermolecular modes of the *neutral* cluster which undoubtedly lead to fragmentation.

As a test of the Gaussian model, the $n = 8$ photoelectron spectrum was fit to a Gaussian profile of the form

$$g(E) = N \exp\{-(E - E_n^0)^2/\sigma^2\} + C \qquad (1)$$

using a nonlinear least squares procedure with the result displayed in Fig. 4. The overall shape of the photoelectron spectrum is indeed well characterized as a Gaussian function, and we associate the E^0 parameter defining the maximum with the vertical electron detachment energy (VDE) for the anion frozen at its equilibrium geometry. This fitting procedure was then applied to the remaining photoelectron spectra and the fitted line shapes are presented in Fig. 3 as the solid curves through the experimental data. The E^0 values are collected in Table I along with each FWHM.

IV. DISCUSSION

The vertical detachment energies are the central results of this study and are plotted as solid points (●) in Fig. 5 as a function of cluster size. The monomer value (■) obtained by Coe et al.[18] is included with the data set extracted from this study. The most striking aspect of these data is the enormous shift in VDE going from monomer to dimer (1.4 vs 2.6 eV, respectively) which is *reversed* at $n = 6$ where the vertical detachment energy is suddenly lowered by almost one electron volt from $n = 5$ to $n = 6$ (3.25 vs 2.49 eV, respectively). The two points given for $n = 6$ arise from the observation that the photoelectron spectrum for this cluster was the only one which could not be reasonably fit to a single Gaussian (see Fig. 6). The $n = 6$ spectrum was therefore fit to a sum of two Gaussians, where the E^0 and σ parameters for the high
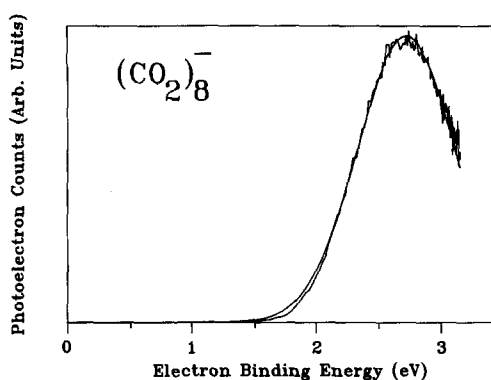

FIG. 4. Expanded spectrum of $(CO_2)_8^-$ with least-squares fit to Gaussian line shape.

TABLE I. Cluster size dependence of the vertical electron detachment energies (VDE), defined as $h\nu - E_n^0$, and FWHM values obtained by fitting the photoelectron spectra to the Gaussian line shape function $g_n(E) = N\exp\{-(E - E_n^0)^2/\sigma_n^2\} + C$.

$(CO_2)_n^-$	E_n^0 (eV)	VDE = $3.495 - E_n^0$ (eV)	FWHM (eV)
$n = 2$	0.71 (0.02)[a]	2.79 (0.02)	1.07 (0.06)
3	0.56 (0.02)	2.94 (0.02)	1.18 (0.10)
4	0.54 (0.04)	2.96 (0.04)	0.96 (0.06)
5	0.25 (0.02)	3.25 (0.02)	1.06 (0.07)
6	0.10 (0.06)	3.40 (0.06)	0.74 (0.02)
	1.04 (0.10)	2.49 (0.10)	0.83 (0.02)
7	0.93 (0.02)	2.57 (0.02)	0.92 (0.02)
8	0.77 (0.005)	2.73 (0.005)	0.92 (0.01)
9	0.70 (0.02)	2.80 (0.02)	0.87 (0.06)
10	0.66 (0.02)	2.84 (0.02)	0.82 (0.05)
11	0.61 (0.03)	2.89 (0.03)	0.80 (0.05)
12	0.60 (0.03)	2.90 (0.03)	0.73 (0.07)
13	0.55 (0.03)	2.95 (0.03)	0.67 (0.08)

[a] Numbers in parentheses indicate error ($\pm$) in derived quantities.

binding energy Gaussian were varied starting from the values obtained for the $n = 5$ fit. The success of this procedure in recovering the observed line shape suggests that the $n = 6$ spectrum is comprised of two components, one which is a continuation of the trend from $n = 2$ to $n = 5$, and another which is the beginning of a trend extending out to $n = 13$.

The key to interpreting these vertical detachment energies was provided by Fleischman and Jordan[21] who calculated the equilibrium geometries of different conformers of the dimer anion and found two stable forms, shown in Fig. 7. These forms correspond to an essentially ion-induced dipole complex of C_s symmetry [Fig. 7(a)] and the D_{2d} symmetrical dimer [Fig. 7(b)], with the D_{2d} structure predicted to be about 0.2 eV more stable than C_s. While these structures are close in energy, the vertical detachment energies of the two structures are very different (1.7 vs 2.8 eV, respectively) because of the increased distortion of the neutral framework in the D_{2d} geometry compared to C_s. These authors also calculate a vertical detachment energy (VDE) for the CO_2^- monomer of 1.2 eV, in good agreement with the experimental value of Bowen and co-workers[18] of 1.4 eV. Our VDE

value for the dimer anion is 2.79 ± 0.02 eV (Table I), in close agreement with the 2.8 eV value expected for the D_{2d} form. The suggestion that the dimer anion assumes the symmetrical conformation was forwarded by Fleischman and Jordan[21] based on the lower VDE bound of 2.3 eV set by Coe et al.[18] While the near exact agreement between our value and the theoretical prediction is undoubtedly fortuitous, the suggestion of a D_{2d} structure is certainly further supported by our results.

The existence of two possible forms of the dimer anion also provides a context with which to interpret the discontinuity in VDE at $n = 6$ (Fig. 5). Fleischman and Jordan[21] point out in their paper that $(CO_2)_n^-$, $n > 2$ clusters should have two isomeric forms characterized as $CO_2^- \cdot (CO_2)_n$ and $C_2O_4^- \cdot (CO_2)_{n-1}$. They further speculate that adding subsequent CO_2 ligands would stabilize the CO_2^- core ion more than the D_{2d} $C_2O_4^-$ dimer core, and that the two structures would be nearly isoenergetic at $n = 3$. We would expect to observe such a change in core ion by the 1.1 eV difference between the VDE values of the two possibilities, assuming that the difference in CO_2 monomer binding energies is small compared to 1.1 eV. Such binding energies are known[6]
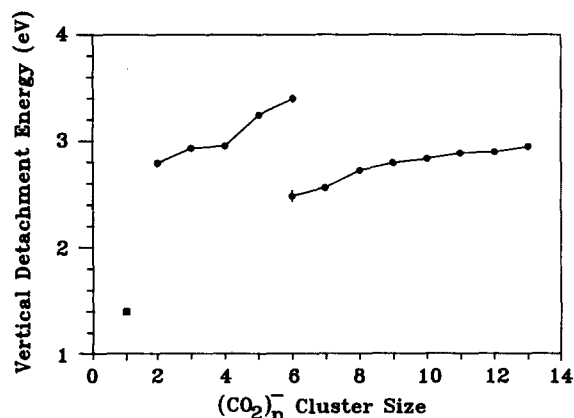
FIG. 5. Plot of the fitted peaks of the spectra, E_n^0, taken as a measure of the vertical detachment energy (filled circles). The monomer value (filled square) is taken from Coe et al. (Ref. 18). Error bars (standard deviation of fit) larger than the plotted points are shown.
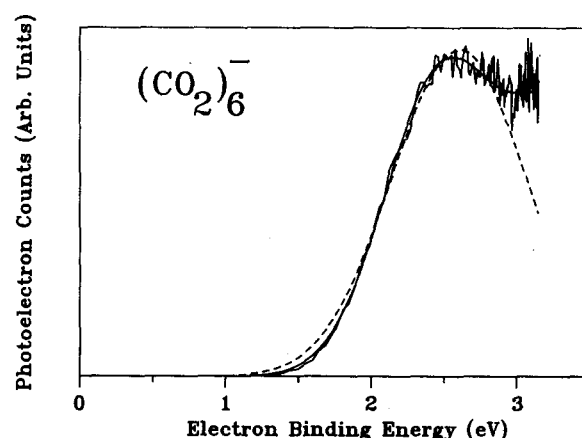
FIG. 6. Expanded spectrum of $(CO_2)_6^-$ with fit to sum of two Gaussians (solid line) and one Gaussian (dashed line).
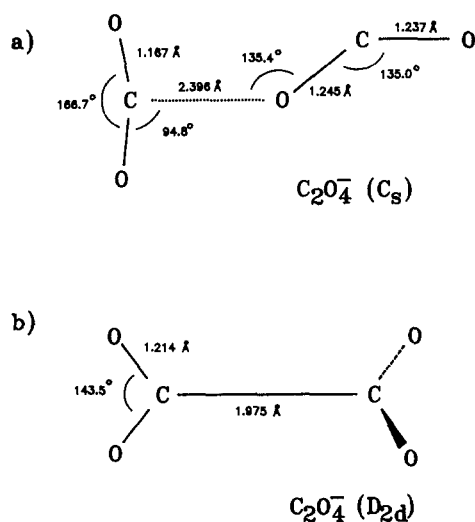
FIG. 7. Structures for CO_2 dimer anion conformations calculated by Fleischman and Jordan (Ref. 21): (a) C_s or ion–solvent structure, and (b) symmetrical D_{2d} structure.

to rapidly approach 0.22 eV, close to the bulk energy of vaporization of dry ice (0.25 eV). The *difference* in monomer binding energies of the two conformers will be much smaller that this value so that a VDE shift on the order of 1 eV should reveal a change in core ion.

The cluster size dependence of the VDE values shown in Fig. 5 reveals that from $n = 2$ to $n = 5$ the VDE increases by 0.1 eV with each additional solvent molecule, except for a small deviation at $n = 4$. We conclude that clusters in this range maintain a dimer core ion which is weakly solvated with each additional CO_2. The hexamer presents an anomaly as the VDE shifts 0.76 eV *lower* in energy when compared to $n = 5$ (see Fig. 5), a jump which cannot be explained as a solvation effect. The direction and magnitude of this shift is, however, consistent with a change in conformation from the highly distorted dimer anion core to the solvated monomer ion form. The predicted 1.1 eV shift described above, which relates only to two conformers of a given cluster size, is in fact recovered in the VDE *difference* between the two observed components of $n = 6$ (0.91 $\pm$ 0.16 eV). For $n > 6$, the sequential VDE values again shift slowly toward higher binding energy, as expected for incremental solvation of a common core ion. The asymptotic behavior observed where the vertical detachment energy becomes independent of cluster size is expected when the CO_2 monomer binding energy is the same for ionic and neutral clusters. Lineberger and co-workers[6] have shown that the CO_2 binding energies onto both positively[26] and negatively[27] charged CO_2 clusters approach the bulk heat of evaporation of dry ice for cluster sizes larger than about 10. *Summarizing, the cluster size dependence of the VDE values imply that the D_{2d} dimer forms the core of the clusters from $n=2$ to $n=5$ while $n>6$ clusters occur with the charge localized on a CO_2 monomer.*

Interestingly, this interpretation of the data leads to the conclusion that two conformers of the hexamer exist simultaneously and suggests that this is the cluster size for which the two forms are isoenergetic rather than $n = 3$ as speculat-

ed by Fleischman and Jordan[21]. This propensity of CO_2 clusters to form multiple conformers has actually been observed previously by Kafafi *et al.*[28] who studied the infrared spectra of matrix isolated $Li^+C_2O_4^-$. They find evidence for a symmetrical form of $C_2O_4^-$ which can be photolytically converted to a $Li^+CO_2^- \cdot CO_2$ ion–molecule complex.

If two isomeric forms are indeed in competition as a function of cluster size, it seems that the mix of the two isomers for $n = 6$ as well as the $2 \leqslant n \leqslant 5$ vs $n > 6$ intensity ratio should depend on the detailed source conditions. In a preliminary attempt to identify whether the abundance of each conformer can be manipulated in the isolated clusters, consider the cluster distribution shown in Fig. 2(a) using near zero energy electrons. In this source configuration the $n \geqslant 7$ clusters are favored with minor contributions from $n = 5$ and $n = 6$. It is plausible that low energy electron attachment preferentially leads to monomer anion based clusters owing to a barrier in the formation of the smaller $2 \leqslant n \leqslant 6$ dimer based clusters. Such a barrier may result from the strong distortion of the neutral framework required to approach the D_{2d} dimer anion geometry as evidenced by its high vertical detachment energy. This propensity of smaller anion clusters requiring high electron energy (a few electron volts) to form has been observed previously by Stamatovic *et al.*[3] and Knapp *et al.*[24] in studies of the electron energy dependence of $(CO_2)_n^-$ formation. In another study, Kondow and Mitsuke[5] have observed the cluster size distribution from transfer of a rare gas Rydberg electron and find that $n = 7$ is the smallest formed, again showing that low energy electron processes preferentially generate monomer ion based clusters. In light of this suggestion that different electron energies yield clusters of differing compositions, it will be interesting to probe the weak $n = 5$ and $n = 6$ ions prepared by low energy electron attachment [Fig. 2(a)] to see if the shape of their photoelectron spectra are dependent on source conditions. These measurements are currently underway in our laboratory. In addition this system appears ideal for the application of vibrational photofragmentation spectroscopy as the characteristic frequencies of each core ion are quite different.[21]

V. CONCLUSIONS

The 3.49 eV photoelectron spectra of $(CO_2)_n^-$, $2 \leqslant n \leqslant 13$ were recorded and analyzed to obtain the cluster size dependence of the vertical electron detachment energies (VDE). These VDE measurements reveal two sharp discontinuities occurring at $n = 2$ and $n = 6$ which are interpreted using the *ab initio* results of Fleischman and Jordan.[21] Comparison of the direction and magnitude of the discontinuous shifts with the difference in VDE expected for two calculated conformers of the dimer anion indicate that the D_{2d} symmetrical conformer forms the core ion for clusters with $2 \leqslant n \leqslant 6$ and the monomer resides at the core of $n \geqslant 6$. It is possible that two conformers of the hexamer anion coexist under our source conditions.

An interesting aspect of these results is that rather large changes (≈ 1 eV) occur in the photoelectron spectrum from $n = 5$ to $n = 6$, while no strong magic numbers have been reported previously at these cluster sizes. Alexander *et al.*[6]

report intensity anomalies in the mass spectrum at $n = 4, 7,$ 10, and 14, while the photoelectron spectra are smoothly varying from $n = 7$ to $n = 13$. It therefore appears that the *large structural changes clearly evidenced in photoelectron spectroscopy are essentially absent in the mass spectrum,* indicating that some caution should be exercised when attempting to extract structural information from ion intensity information alone. Unfortunately, the strong magic number at $n = 14$, which always appears in $(CO_2)_n^-$ mass spectra, could not be directly probed using pulsed photoelectron spectroscopy owing to the propensity of this cluster to undergo photodissociation with 355 nm excitation.[6]

ACKNOWLEDGMENTS

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