Electron Attachment to CO₂ Embedded in Superfluid He Droplets

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ABSTRACT: Electron attachment to CO₂ embedded in superfluid He droplets leads to ionic complexes of the form (CO₂)₂− and (CO₂)O− and, at much lower intensities, He containing ions of the form He₅(CO₂)O−. At low energies (< 5 eV), predominantly the non-decomposed complexes (CO₂)₂− are formed via two resonance contributions, similar to electron attachment to pristine CO₂ clusters. The significantly different shapes and relative resonance positions, however, indicate particular quenching and mediation processes in CO₂@He. A series of further resonances in the energy range up to 67 eV can be assigned to electronic excitation of He and capture of the inelastically scattered electron generating (CO₂)₂− and two additional processes where an intermediate formed He⁶ leads to the nonstoichiometric anions (CO₂)O−.

INTRODUCTION

Electron attachment to CO₂ embedded in superfluid He droplets (CO₂@He) is studied in a crossed beams experiment with mass spectrometric detection of the anions. Over the past few years electron attachment and/or electron ionization for a variety of molecules embedded in He droplets, including H₂O, CH₃Cl, and more complex systems like the explosive trinitrotoluene (TNT)³ or building blocks of life such as fullerenes and various low-mass molecules⁷ have been studied in our laboratory. It has been shown that He droplets provide excellent conditions to generate relaxed parent anions, which are not observed in free electron attachment experiments with the corresponding gas phase molecules. The general behavior for a molecule embedded in a helium droplet is that the dissipative environment suppresses dissociative electron attachment (DEA) in favor of associative attachment (AA, formation of the parent anion). In extreme cases, DEA can be suppressed completely and only intact anions are generated. This is the case, e.g., when DEA to the isolated molecule is suppressed completely and only intact anions are generated. In this case the rich fragmentation patterns, partly due to metastable decompositions (processes occurring on the microsecond time scale) being completely suppressed in favor of AA when going from the isolated molecule to TNT@He.³ In addition, He droplets serve as a cryogenic nanolaboratory to study processes at temperatures close to zero K.¹²

Electron scattering from CO₂ and DEA to CO₂ has a long and interesting history owing to the fact that linear CO₂ becomes bent when attaching an electron and thereby generating CO₂−. Interestingly, in spite of extensive research, the exact number of the most fundamental quantity connecting the ground state molecule with its anion, namely the (adiabatic) electron affinity of CO₂ (corresponding to the (adiabatic) electron binding energy of CO₂−) is still under question. The most recent high-level ab initio calculations¹³ predict that the O–C–O angle decreases from 180° to 138°, while the bond distance increases from 117 to 124 pm when changing from the neutral to the anion. The energy of ground state CO₂− is predicted to be 0.6 eV above that of the neutral, indicating that CO₂− is metastable and the adiabatic electron affinity of CO₂ is negative (−0.6 eV). On the other hand, there are hints from photodetachment spectroscopy that the electron affinity of CO₂ might be positive.¹⁴

Electron scattering from gas phase CO₂ exhibits a structured resonant feature centered at 3.7 eV, which is assigned as a 1Π shape resonance due to accommodation of the extra electron into the lowest unoccupied molecular orbital (MO) with antibonding π* character.¹⁵,¹⁶ These structures are identified as symmetric stretch vibrations in the transitory anion (CO₂−), also referred to as boomerang structures. The term boomerang is based on the idea that in the transient anion (TNI) only one reflection of the nuclear wave packet occurs along the symmetric stretch before it is annihilated by autodetachment. The resonance position further indicates that the vertical attachment energy (3.7 eV) is considerably larger than the
energy to generate \( \text{CO}_2^- \) in its equilibrium geometry, which is also expected from the large geometry change between the neutral and the anion as mentioned above.

Negative ion formation in electron capture by single gas phase \( \text{CO}_2 \) yields \( \text{O}^- \) as the only observable negative ion.\(^{15,18} \)

The energetic threshold for \( \text{O}^- \) formation (at 300 K) is at 4.0 eV,\(^{15} \) and hence DEA is energetically only accessible from the higher energy side of the \( ^2\Sigma_u^- \) resonance. The further resonance contribution at 8.2 eV is due to DEA involving a core excited resonance.

More than three decades ago, \( \text{CO}_2 \) was among the first systems where negative ion formation in electron attachment to homogeneous clusters was studied. These earlier studies (at poor electron energy resolution) indicated the formation of non-decomposed complexes of the form \( \text{(CO}_2)_n^- \) below 4 eV and products of the form \( \text{(CO}_2)_n\text{O}^- \) within the energy domain of the \( ^2\Pi_u \) resonance.\(^{20-25} \)

Later, a study at ultrahigh resolution (1 meV, laser photoelectron attachment) revealed sharp structures in the energy range between threshold and 180 meV observed on the products \( \text{(CO}_2)_n^- \).\(^{24} \) These structures were identified as vibrational Feshbach resonances (VFRs) involving symmetric stretch and bending vibrations.\(^{25} \) Vibrational Feshbach resonances at energies up to 0.5 eV could also be identified in a high-resolution (0.1 eV) study on electron attachment to \( \text{CO}_2 \) clusters recently performed by our laboratory.\(^{26} \)

Here we explore electron attachment to \( \text{CO}_2\text{He} \) in the energy range 0–67 eV. Under typical experimental conditions \( \text{He} \) droplets are usually doped with several molecules, which will lead to cluster formation inside the droplet and hence not only electron attachment to single \( \text{CO}_2 \) molecules but also the results from electron attachment to clusters are important for the interpretation of the present results. As will be shown, effective electron attachment takes place in the energy range below 5 eV, similar to pristine \( \text{CO}_2 \) clusters. In addition, further strong resonance features are observed in the range up to 67 eV, which can be assigned to electronic excitation of \( \text{He} \) and subsequent attachment of the slowed down electron forming \( \text{(CO}_2)_n^- \) as well as a second process where an intermediate \( \text{He}^* \) is colliding with the neutral \( \text{CO}_2 \) cluster and forms predominantly the nonstoichiometric ions \( \text{(CO}_2)_n\text{O}^- \).

### EXPERIMENTAL SECTION

The present measurements are performed with a \( \text{He} \) droplet source combined with a pickup cell containing \( \text{CO}_2 \), an ion source and a mass spectrometer system to analyze the resulting anions. The helium droplet beam is formed by expansion of \( \text{He} \) through a nozzle of 5 \( \mu \text{m} \) diameter into vacuum at a temperature between 8 and 13 K and a pressure of typically 23 bar. Under these operating conditions the mean size of the helium droplets is between \( 10^6 \) and \( 10^7 \). At a distance of 1 cm downstream, the \( \text{He} \) droplets pass a skimmer before they enter a differentially pumped pickup cell. About 20 cm further downstream the \( \text{CO}_2 \) doped helium droplet beam enters the collision chamber of an ion source where free electron attachment to the doped droplets takes place. In the present study we utilize either a commercial Nier-type ion source (electron energy resolution about 1 eV) in combination with an orthogonal time-of-flight mass spectrometer\(^{1} \) or a home-built hemispherical electron monochromator (electron energy resolution around 100 meV) equipped with a quadrupole mass filter and channel electron multiplier.\(^{27} \) The electron energy scale is calibrated by measuring the well-known narrow resonance in \( \text{SF}_6 \) close to 0 eV leading to the parent anion \( \text{SF}_6^- \) under identical conditions.

### RESULTS AND DISCUSSION

For the isolated \( \text{CO}_2 \) molecule \( \text{O}^- \) is the only DEA product, which is formed via two pronounced resonances at 4.4 and 8.2 eV\(^{26} \) due to the DEA reaction

\[
e^- + \text{CO}_2 \rightarrow \text{CO}_2^- \rightarrow \text{O}^- + \text{CO}
\]

with \( \text{CO}_2^- \) the transient negative ion initially formed upon electron attachment. The low-energy peak is associated with the \( ^2\Sigma_u^- \) shape resonance and the one at higher energy with an electronically excited Feshbach resonance. This excited resonance decomposes by releasing appreciable translational energy but also vibrational excitation in \( \text{CO} \) (up to \( v = 21 \)).\(^{18} \)

Similar to the \( \text{CO}_2 \) clusters,\(^{20} \) electron attachment to \( \text{CO}_2\text{He} \) leads to the two series of ions, namely the non-decomposed complexes of the form \( \text{(CO}_2)_n\text{O}^- \) \((n > 1)\) and solvated fragment ions of the form \( \text{(CO}_2)_n\text{O}^- \) \((n > 0)\). In addition, \( \text{He} \) containing complexes of the composition \( \text{He}_m\text{(CO}_2)_n\text{O}^- \) are generated.

Figure 1 displays a mass spectrum in the range between \( \text{(CO}_2)_2\text{O}^- \) \((104 u)\) and the complex \( \text{He}_3\text{(CO}_2)_2\text{O}^- \) \((116 u)\).

![Figure 1](https://example.com/figure1.png)
anions such as OH\(^-\) and F\(^-\) are able to be solvated in \(^4\)He droplets but interact too weakly with the He to lead to magic numbers in cluster size distributions. In contrast, H\(^+\) sits outside the droplets.\(^{31}\) More recent calculations by Huber and Mauracher\(^{32}\) suggest that the metastable anion He\((\ast)^-\) strongly binds to He and prefers a position inside a \(^4\)He droplet whereas the metastable dimer anion He\(_2\)\((\ast)^-\) is heliophobic and weakly binds to the surface of a He droplet. However, the statistical uncertainty for the He\(_n\)(CO\(_2\))O\(^-\) anions does not allow the assignment of a shell closure at a certain number of He atoms, as reported recently for halogen anions.\(^{28}\) Furthermore, the superposition of isobaric anions (both \(^{12}\)C and \(^{16}\)O are close in mass to a multiple of \(^4\)He) as shown in the inset of Figure 1 provides another challenge to identify magic numbers in the anion series He\(_n\)(CO\(_2\))O\(^-\) (\(n \geq 0\)).

In the following we shall first consider electron attachment to CO\(_2\)@He in the electron energy range below 4 eV, observed on the non-decomposed tetramer ion (CO\(_2\))\(_4\)\(^-\) and recorded at high-electron-energy resolution of about \(\Delta E = 0.1\) eV (FWHM). Subsequently, we shall explore the entire energy range between threshold (near 0 eV) and 67 eV where the non-decomposed complexes (CO\(_2\))\(_n\)\(^-\) and the solvated ions (CO\(_2\))\(_n\)O\(^-\) are formed via a series of resonant processes.

Figure 2 presents a comparison of electron attachment to homogeneous CO\(_2\) clusters (pristine CO\(_2\), top) and electron attachment to CO\(_2\)@He (bottom panel), both observed on the tetramer ion (CO\(_2\))\(_4\)\(^-\). Apparently, the two clearly separated low-energy resonant features from pristine CO\(_2\) do strongly overlap when going to CO\(_2\)@He. One has to keep in mind that the energy scale refers to the kinetic energy of the electrons in a vacuum. Entering the droplet substantially affects both the energy and nature of the excess electron. As discussed earlier in a study on electron capture by pure He droplets,\(^{33}\) electron injection into the bottom of the conduction band in He requires an energy of 1.15 eV (\(V_0 = -1.15\) eV) and subsequent formation of electron bubbles requires some additional activation energy. In light of that, one would expect a shift of about 1.6 eV to higher energies when going from pristine CO\(_2\) to CO\(_2\)@He.

As discussed in detail in our recent study on electron attachment to CO\(_2\) clusters,\(^{26}\) the low-energy (<0.5 eV) ion signal is associated with a so-called virtual state near 0 eV\(^{34,35}\) and the VFRs known from the ultrahigh-resolution experiments on electron attachment to CO\(_2\) clusters.\(^{24}\) This virtual state was introduced in the course of scattering experiments to describe excitation of the infrared inactive symmetric stretching mode in the threshold region. The feature between 1 and 4 eV consists of three overlapping resonances with maxima at 1.4, 2.2, and 3.1 eV. The resonance near 2.2 eV (not seen in electron attachment to single CO\(_2\)) can be assigned to a resonant scattering feature recently explored in electron scattering to single CO\(_2\).\(^{36}\) In CO\(_2\) two quanta of the bending vibration (82.7 meV) are accidentally nearly degenerate with one quantum of the symmetric stretch vibration (165.8 meV). The coupling results in two vibrational states (a Fermi dyad) at 159 and 172 meV, each of them represents a mixing of bend vibration and symmetric stretch vibration. In the region between the virtual state and 2.5 eV (where no resonance mechanism was proposed so far) excitation of the higher member of the dyad exhibits a remarkable intensity with a broad resonant shape (indicative of a \(\sigma^*\) resonance\(^{36}\)). Consequently, formation of the non-decomposed complexes in that energy region (Figure 2) was associated with this resonant scattering phenomenon.\(^{36}\) The resonance feature with a maximum at 3.1 eV that was assigned to the \(^7\)He resonance, in the cluster environment shifted to lower energy by more than 1 eV.\(^{26}\)

In general, formation of (CO\(_2\))\(_n\)\(^-\) from clusters at low energies (<5 eV) most likely proceeds via the reaction

\[
e^- + (\text{CO}_2)_n \rightarrow (\text{CO}_2)_n^{\#} \rightarrow (\text{CO}_2)_4^{-} + (n-4)\text{CO}_2
\]

with (CO\(_2\))\(_n\)\(^-\)# the transient cluster anion formed upon electron attachment. The relaxation energy to form (CO\(_2\))\(_4\)\(^-\) can be used either to evaporate the target cluster (formation of \((n-4)\) neutral CO\(_2\) molecules) or to split off the neutral complement of the target cluster ((CO\(_2\))\(_{n-4}\)).

The fact that electron attachment to CO\(_2\)@He finally leads to (CO\(_2\))\(_n\)\(^-\) (with only small intensities of He containing ions), means that the droplet either undergoes complete evaporation in the course of the attachment process or splits off into a number of fragments, thereby releasing (CO\(_2\))\(_n\)\(^-\). To evaporate one He atom from the droplet, an energy of 0.6 meV is required, indicating that the complete evaporation of a target cluster (average size \(10^5\) He atoms) on average requires 60 eV, which in turn indicates that the target cluster does not completely evaporate. Open shell anions such as (CO\(_2\))\(_n\)\(^-\) may show a similar interaction with the superfluid He as a free electron, i.e., formation of a bubble and heliophobic character. Another possibility for large droplets is the high probability for two or more electrons entering the droplet and subsequent Coulomb repulsion between the dopant anion (CO\(_2\))\(_n\)\(^-\) and possible electron bubbles pushing all but one negatively charged species out of the droplet.

Figure 2 indicates that the low-energy contribution (<0.5 eV) and the higher energy feature (composed of contributions from the Fermi dyad) do overlap in CO\(_2\)@He having maxima at 1.8 and 3.1 eV. The first resonance shows the expected shift of about 1.6 eV and a substantial broadening, which prevents the observation of the doublet clearly seen from pristine CO\(_2\).
clusters. A two-Gaussian fit to the anion yield of the CO$_2$ tetramer anion from pristine CO$_2$ clusters as shown in ref 26 leads to peaks centered at 2.2 and 3.2 eV. However, these peaks do not lead to corresponding peaks in the CO$_2$@He case, shifted by 1.6 eV. The asymmetric peak shape suggests an additional contribution at the low-energy side, and by fitting the ion yield of the tetramer anion from pristine CO$_2$ clusters with three Gaussian peaks, we find for the CO$_2$@He corresponding peaks for the two first shifted by 1.6 eV. The width and the shifted position of the resonances agree very well for the two anion efficiency curves; however, the intensity of the resonances at higher electron energies are strongly suppressed for CO$_2$-doped He droplets. All resonances for dopant anions from doped He nanodroplets measured so far have shown a shift of about 1.6 eV, which supports the present approach to add an additional low-energy resonance. Measurements of anion efficiency curves from He nanodroplets doped with other species with high-electron-energy resolution are necessary to provide a clear answer for this unexpected behavior of the shift of the anion yield that is assigned to the Fermi dyad and the $^2$II$_u$ resonance for (CO$_2$)$_n^-$ anions formed via electron attachment to pristine CO$_2$ clusters.

On the basis of the present material, one can tentatively interpret this rather unexpected result by supposing that in CO$_2$@He the contribution from the $^2$II$_u$ resonance is strongly suppressed while the contribution from the Fermi dyad is mediated in CO$_2$@He, thereby extending to lower energies and finally resulting in a resonant feature peaking at 3.1 eV and a much weaker contribution at 3.8 eV. It should be noted that the scattering experiments on single CO$_2$ revealed effective excitation of the higher members of the Fermi dyad in the entire energy range between the virtual state and about 2.5 eV.

The relative intensities of the two contributions of the (CO$_2$)$_4^-$ anion efficiency curve are significantly affected when the nozzle temperature is changed between 10 and 11 K in the way that the ratio between the contributions at 1.8 eV to that at 3.1 eV (and 3.8 eV) is increased from 0.7 to 1.6. (Figure 3).

Figure 3. Electron attachment to CO$_2$@He leading to (CO$_2$)$_4^-$ at two nozzle temperatures ($\Delta E = 0.1$ eV, $P_{He}= 20$ bar, $I_d = 8$ nA, $p_{CO_2} = 6$ mPa).

The increase of the nozzle temperature results in a decrease of the mean droplet size from about $1.4 \times 10^3$ to about $1.8 \times 10^4$ He atoms. This behavior may simply reflect the fact that the larger droplet provides better means to dissipate excess energy and hence the relative intensity of the higher energy resonance is increased with the size of the droplet.

The upper diagram of Figure 4 shows ion yield curves for the anion (CO$_2$)$_{10}^-$ (dashed line) and that of the complex (CO$_2$)$_n^-$ (solid line) in an extended energy region up to 67 eV recorded with the low-electron-energy-resolution device.

Figure 4. Ion yield of CO$_2$O$^-$ (solid line) and the non-decomposed tetramer anion (CO$_2$)$_{10}^-$ (dashed line) in the extended electron energy range up to 67 eV recorded at low-electron-energy resolution ($\Delta E = 1$ eV, $T_{He} = 9.7$ K, $P_{He} = 23$ bar, $I_d = 45$ $\mu$A, $p_{CO_2} = 6$ mPa). The lower diagram shows the sum of the anion yields of the series (CO$_2$)$_n^-$ (solid line) and the series of the stoichiometric anion series (CO$_2$)$_{n-1}^-$ (dashed line). In the inset of the lower diagram the ion yield up to 4 eV for the two ion series is shown with the yield of the sum of the (CO$_2$)$_n^-$ anion series multiplied with 0.1 for a better comparison. Both curves can be reproduced by a two-Gaussian fit, as shown for the sum of the nonstoichiometric anion series (solid line).

The lower diagram shows the sum of the non-decomposed anions (CO$_2$)$_n^-$ (dashed line, $n = 2$–16) and the sum of the nonstoichiometric anions (CO$_2$)$_n^-$ (solid line, $n = 1$–15). Resonant structures located near 2 eV (predominantly yielding the non-decomposed ions (CO$_2$)$_n^-$) as well as around 13, 22, 35, 44, and 57 eV are visible. Negative ion formation within the first broad resonance can be associated with both low-energy features from Figure 2 (bottom), namely ion formation (a) via the virtual state and the vibrational Feshbach resonances and (b) via the Fermi dyad. Owing to the poor energy resolution, these two features are no longer separated. Whereas for CO$_2$O$^-$ the 2 eV resonance is completely missing, fragment anions of larger clusters can be formed at this energy, although at much lower intensity than at higher electron energies. Furthermore, the 2 eV feature for both the stoichiometric and the nonstoichiometric CO$_2$ cluster anions exhibits two contributions at 0.6 and 2.3 eV with substantially higher intensity at the higher energy (see inset in the lower diagram of Figure 4). This suppression of the low-energy feature agrees very well with the temperature and pressure dependence reported for pristine (CO$_2$)$_4^-$ from pristine CO$_2$ clusters. Taking into account space charging by the 45 $\mu$A electron beam, these two energies can be assigned to the resonances at 1.7 and 3.1 eV measured with high resolution (Figures 2 and 3). At these low energies the additional energy required to dissociate one CO$_2$ molecule is provided by the solvation of the anion in a large enough number of CO$_2$ molecules. In the present data we observe an increase of the red shift of the low-energy resonances with increasing cluster size and the feature seen at 0.6 eV in the inset of the lower panel of Figure 4 is only present for O$^-$ that is solvated by more than five CO$_2$ molecules. Anion formation
within the second resonance feature peaking near 13 eV can be assigned to the electronically excited resonances known from single CO\textsubscript{2} (see relative cross section of O\textsuperscript{−} formation in ref 26) but also further electronically excited resonances that are known from condensed phase experiments. Electron stimulated desorption (ESD) of O\textsuperscript{−} from condensed phase CO\textsubscript{2} shows a series of strong resonances in the energy region above 10 eV\textsuperscript{37}. One can assume that the surrounding He matrix substantially decreases the autodetachment of these excited resonances (not present in DEA to single molecules) to a degree that they become visible in the desorption of fragment anions.\textsuperscript{38}

The third feature for negative ion formation around 22 eV roughly coincides with the energy range observed in the formation of negatively charged pure He droplets.\textsuperscript{33} We accordingly propose that negative ion formation in that domain is mediated by electronic excitation of He, i.e., electronic excitation of He and attachment of the slowed down electron to CO\textsubscript{2}. From the fact, however, that also DEA takes place (formation of (CO\textsubscript{2})\textsubscript{n}O\textsuperscript{−}) we propose that in addition to capture of inelastically scattered low-energy electrons, two further mechanisms are operative, resulting in the formation of the solvated ion complexes, namely Penning ionization and DEA induced by coupling of CO\textsubscript{2} to electron-exciton complexes in He. Penning ionization of CO\textsubscript{2} via the He (1s2s) metastable states \textsuperscript{3}S and \textsuperscript{3}P creates electrons at energies in the range below 6 eV (depending on the amount of energy that remains in the CO\textsubscript{2} cluster) which can induce DEA in CO\textsubscript{2} molecules:\textsuperscript{39,40}

$$e^{-}(22 \text{ eV}) + \text{He} \rightarrow \text{He}^{+} + e^{-}(2.2 \text{ eV}) \quad (3a)$$

$$\text{He}^{+} + (\text{CO}_2)\text{m} \rightarrow \text{He} + (\text{CO}_2)\text{m−1}^{+} + (\text{CO}_2)_{i} + e^{-}(\text{<6} \text{ eV}) \quad (3b)$$

$$\text{CO}_2\text{i} + e^{-} (\sim 4 \text{ eV}) \rightarrow (\text{CO}_2)\text{m}^{+} \text{O}^{-} + \text{CO}(\text{CO}_2)\text{m−1} \quad (3c)$$

The second and probably dominant mechanism involves electron-exciton resonances, which are the condensed phase analogues to the well-known He\textsuperscript{−} resonances with the lowest He\textsuperscript{−} (1s2s2p) Feshbach resonance, located 0.5 eV below the lowest excited neutral, He(1s2s\textsuperscript{3}S)

$$e^{-}(22 \text{ eV}) + \text{He} \rightarrow \text{He}^{+} + e^{-}(2.2 \text{ eV}) \rightarrow \text{He}^{−} \quad (4a)$$

$$\text{He}^{−} + (\text{CO}_2)\text{m} \rightarrow \text{He} + (\text{CO}_2)\text{m−1} \text{CO}^{+} + (\text{CO}_2)_{i} \text{O}^{-} \quad (4b)$$

From electron stimulated desorption of molecules on rare gas films, these substrate mediated DEA processes can be observed as strong enhancements in the fragment ion desorption yield at the energy of the electron-exciton resonances.\textsuperscript{41}

Anion formation within the feature around 35 eV can be considered in analogy to the processes discussed for the 13 eV resonance region, scaled to higher energy by the excitation energy of He. In other words, inelastic scattering from He leads to attachment of electrons in the energy range around 13 eV to CO\textsubscript{2} via electron excited resonances.

Figure 5 displays the intensity distributions of the series (CO\textsubscript{2})\textsubscript{n}\text{O}^{-} (open circles) recorded at 13 eV and that of (CO\textsubscript{2})\textsubscript{n}^{-} (solid squares) recorded at 2 eV electron energy. It should be noted that these spectra do not represent the raw data. All contributions from different isotopomers for a given anion were added up. In the anion spectrum obtained at 13 eV the peaks due to the stoichiometric anions and those due to products of the form He\textsubscript{m}(CO\textsubscript{2})\textsubscript{n}\text{O}^{-} are suppressed. The inset in the upper panel of Figure 5 shows the ion yields for cluster sizes up to n = 20. Whereas the monomer anion CO\textsubscript{2}^{-} cannot be found at all and the dimer (CO\textsubscript{2})\textsubscript{2}^{-} is only slightly larger than the noise, the trimer is clearly visible in the mass spectrum. High-level ab initio calculations predict that the tetramer is at the brink of stability.\textsuperscript{32} We can therefore assume that the intensity distribution of (CO\textsubscript{2})\textsubscript{n}^{-} reflects the stability of these anions in the He droplet; i.e., the monomer and dimer may be metastable but the larger cluster anions do possess appreciable binding energies for the excess electron (positive electron affinities). Both cluster size distributions exhibit pronounced intensity anomalies (magic numbers) that are also known from cluster size distributions obtained via electron attachment to pristine CO\textsubscript{2} clusters.\textsuperscript{43,44} To compare the present mass spectrum of the (CO\textsubscript{2})\textsubscript{n}^{-} anions with cluster size distributions published in the literature,\textsuperscript{43,44} we plotted the difference of measured anion yields (upper panel) and a strongly smoothed fit to this curve in comparison to equally treated data published in the literature.\textsuperscript{43,44}
He and boils off 1600 He atoms for each 1 eV of released energy. Thus, the magic numbers in the present experiment originate solely from the ionization process and it is interesting to note that even superfluid He is not able to carry away the excess energy that is released in the ionization event (even at the lowest electron energy of 2 eV).

In summary electron attachment to CO$_2$@He results in ionic complexes of the form (CO$_2$)$_n^-$ and (CO$_2$)$_n$O$^-$, similar to electron attachment to clusters of CO$_2$. The shape of the cross section for the formation of (CO$_2$)$_n^-$ indicates a substantial effect of the He environment indicating particular quenching and mediation process in CO$_2$@He, which have to be explored in more detail by additional studies at high-electron-energy resolution. The series of further resonances in the energy range up to 67 eV are due to (sequential) inelastic scattering of the electron from He and attachment of the slowed down electron leading to resonances 22 eV and multiples of 22 eV above the first resonance. The only exception is a strong resonance at 22 eV for the nonstoichiometric anions (CO$_2$)$_n$O$^-$ which does not have a counterpart at 2 eV at least for n = 1. Two processes where an immediately formed He$^-$ leads to the nonstoichiometric anions (CO$_2$)$_n$O$^-$ at 22 eV are proposed as the inelastically scattered electron with its remaining kinetic energy of only 2 eV cannot lead to dissociative electron attachment to CO$_2$ clusters.

**AUTHOR INFORMATION**

**Notes**
The authors declare no competing financial interest.

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