

High resolution electron attachment to CO₂ clusters

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Electron attachment to CO₂ clusters performed at high energy resolution (0.1 eV) is studied for the first time in the extended electron energy range from threshold (0 eV) to about 10 eV. Dissociative electron attachment (DEA) to single molecules yields O[−] as the only fragment ion arising from the well known ²Π_u shape resonance (ion yield centered at 4.4 eV) and a core excited resonance (at 8.2 eV). On proceeding to CO₂ clusters, non-dissociated complexes of the form (CO₂)_n[−] including the monomer CO₂[−] are generated as well as solvated fragment ions of the form (CO₂)_nO[−]. The non-decomposed complexes appear already within a resonant feature near threshold (0 eV) and also within a broad contribution between 1 and 4 eV which is composed of two resonances observed for example for (CO₂)₄[−] at 2.2 eV and 3.1 eV (peak maxima). While the complexes observed around 3.1 eV are generated *via* the ²Π_u resonance as precursor with subsequent intracluster relaxation, the contribution around 2.2 eV can be associated with a resonant scattering feature, recently discovered in single CO₂ in the selective excitation of the higher energy member of the well known Fermi dyad [M. Allan, *Phys. Rev. Lett.*, 2001, **87**, 0332012]. Formation of (CO₂)_n[−] in the threshold region involves vibrational Feshbach resonances (VFRs) as previously discovered *via* an ultrahigh resolution (1 meV) laser photoelectron attachment method [E. Leber, S. Barsotti, I. I. Fabrikant, J. M. Weber, M.-W. Ruf and H. Hotop, *Eur. Phys. J. D*, 2000, **12**, 125]. The complexes (CO₂)_nO[−] clearly arise from DEA at an individual molecule within the cluster involving both the ²Π_u and the core excited resonance.

Introduction

Electron scattering from CO₂ and dissociative attachment (DEA) to CO₂ has a long and particular history due to the fact that linear CO₂ becomes considerably bent when adding an electron. Interestingly, the most essential quantity of the anion, namely the electron binding energy of the ground state CO₂[−] (corresponding to the adiabatic electron affinity of CO₂) is still under question. According to the most recent high level *ab initio* calculations¹ the O–C–O angle decreases from 180° to 138°, while the bond distance increases from 117 pm to 124 pm on going 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.² CO₂ was among the first systems where negative ion formation upon low-energy electron impact to clusters was studied.^{3,4}

Here we present the first beam experiment on electron attachment to CO₂ clusters in the energy region 0–10 eV performed at high energy resolution (0.1 eV). Before considering

these results we shall briefly recall the essential features known so far concerning electron scattering and electron attachment to CO₂ and its homogeneous clusters.

Electron scattering from gas phase CO₂ exhibits a structured resonant feature centered at 3.7 eV, which is assigned as a ²Π_u shape resonance due to accommodation of the extra electron into the lowest unoccupied molecular orbital (MO).^{5,6} The structures are identified as symmetric stretch vibrations in the transitory anion (CO₂^{−#}), also assigned as *boomerang* structures. The term boomerang is based on the idea that in the transient anion only one reflection of the nuclear wave packet occurs along the symmetric stretch after 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 CO₂[−] in its equilibrium geometry, which is also expected from the large geometry change between neutral and anion. Scattering experiments further indicate a so called *virtual state* near 0 eV,^{7,8} which was introduced to describe excitation of the infrared inactive symmetric stretching mode in the threshold region.

Experiments at much improved energy resolution (7 meV FWHM) studying the excitation of Fermi coupled vibrations revealed new and surprising features in the energy range between the virtual state (near 0 eV) and the ²Π_u resonance.⁹ In CO₂, 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 and symmetric stretch.

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The lower energy member of the dyad is characterized by the large probability to find the molecule either linear and stretched or squeezed and bent. In contrary the upper member is characterized by the large possibility to find the molecule either bent and stretched or squeezed and linear. Stretching and bending motion is in-phase at the upper component of the dyad and out-of-phase in the lower. Due to the much improved energy resolution, the excitation function (the probability to excite a particular vibration as a function of the incident energy) could be recorded separately for both components of the Fermi dyad. The result is a surprising selectivity in the way that in the threshold region below 1 eV excitation of only the higher member shows a prominent peak while the lower member is not excited at all. In the region of the ${}^2\Pi_u$ resonance, the cross sections for the excitation of both members give broad bands, however, with distinct different maxima, namely at 3.5 eV for the higher and 4.2 eV for the lower component of the dyad. The well known boomerang structure is superimposed in both bands. Interestingly, in the intermediate region between the virtual state and the ${}^2\Pi_u$ resonance (between about 1 and 2.5 eV where no resonance mechanism was proposed so far) excitation of the higher member of the dyad exhibits a remarkable intensity. It was proposed⁹ that this broad feature is indicative of a σ^* resonance and both, the π^* and σ^* resonance are subjected to vibronic coupling. As will be shown, this is exactly the energy region where the formation of complexes $(\text{CO}_2)_n^-$ following electron attachment to CO_2 clusters is observed.

Negative ion formation in electron capture by single gas phase CO_2 yields O^- as the only observable negative ion.^{10,11} The energetic threshold for O^- formation (at 300 K) is at 4.0 eV¹² and hence DEA is energetically not accessible from the lower part of the ${}^2\Pi_u$ resonance.

Earlier electron attachment studies to homogeneous CO_2 clusters (at poor electron energy resolution) indicate the formation of non-decomposed complexes of the form $(\text{CO}_2)_n^-$ below 4 eV^{3,4,13,14} and products of the form $(\text{CO}_2)_n\text{O}^-$ within the energy domain of the ${}^2\Pi_u$ resonance. A recent study at ultrahigh resolution (1 meV, laser photoelectron attachment (LPA)) revealed sharp structures in the energy range between threshold and 180 meV observed on the products $(\text{CO}_2)_n^-$.¹⁵ These structures are identified as vibrational Feshbach resonances (VFRs) involving symmetric stretch and bending vibrations.¹⁶ They are significantly red-shifted with the size of the observed cluster ion resulting from the increasing binding energy of the excess electron.

In this contribution we study negative ion formation following electron attachment to CO_2 clusters at high resolution with particular emphasis on the energy range between threshold and the ${}^2\Pi_u$ resonance.

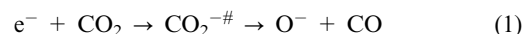
Experimental

Electron attachment to CO_2 clusters is performed by means of the high resolution attachment spectrometer described previously,¹⁷ now combined with a cluster source generating a supersonic beam containing a distribution of neutral clusters. The cluster beam is formed by expansion of CO_2 through a nozzle of 20 μm diameter into vacuum at variable

temperatures and pressures between 2 and 5 bar. The electron beam is formed in a custom built hemispherical electron monochromator, operated at an energy resolution of 90–120 meV (full width at half maximum, FWHM) and an electron current of 5–8 nA. Negative ions formed in the collision zone are extracted by a weak electric field towards the entrance of the quadrupole mass spectrometer. The mass-selected negative ions are detected by a channel electron multiplier using a single pulse counting technique. The intensity of a particular mass-selected negative ion is then recorded as a function of the electron energy. Energy calibration was performed using the well known s-wave resonance of Cl^-/CCl_4 near zero eV.

Results and discussion

Before discussing electron attachment to CO_2 clusters we first present the yield of O^- under expansion conditions where no cluster formation takes place (see Fig. 1). As already known from the earlier studies^{10,11} O^- is generated *via* two pronounced resonances peaking at 4.4 eV and 8.2 eV due to the (DEA) reaction



The low energy peak is associated with the ${}^2\Pi_u$ shape resonance mentioned above and that at higher energy with an electronically excited Feshbach resonance. This excited resonance decomposes by releasing appreciable translational energy but also appreciable vibrational excitation in CO up to $v = 21$.¹¹

As mentioned above, the electron transmission spectrum (ETS)^{5,6} exhibits structures within the ${}^2\Pi_u$ shape resonance identified as vibrations in the transient anion $\text{CO}_2^{-\#}$. These boomerang structures are also weakly visible on the O^- yield provided that the detection efficiency is independent on the translational energy of the O^- ion.¹¹ As nicely demonstrated by Dressler and Allan,¹¹ it is also possible to obtain structures in the O^- yield due to vibrational excitation of the neutral CO fragment. In this case, however, under conditions when only O^- ions with zero kinetic energy are detected. The excess energy of the DEA process (1) (*i. e.*, the difference between electron energy and thermodynamic threshold) is shared between the translational and internal energy of the fragments. With increasing electron energy, successive population of

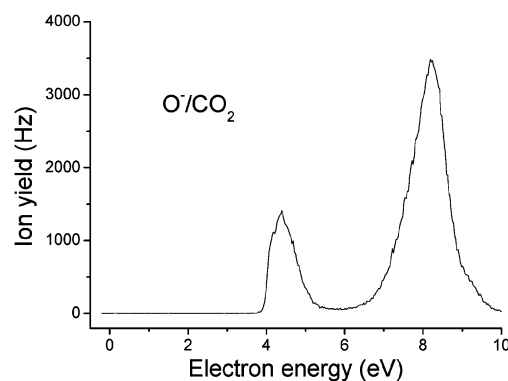


Fig. 1 Formation of O^- from single CO_2 . The contribution peaking at 4.4 eV is assigned to the ${}^2\Pi_u$ resonance and that at 8.2 eV to a core excited resonance (see the text).

vibrational levels in CO will modulate the translational energy of the dissociating particles $\text{O}^- + \text{CO}$. Thus in the zero kinetic energy mode, the O^- ion yield curve exhibits a series of 5 peaks separated by 0.27 eV due to population of the vibrational levels $v = 0-4$ in CO. Conversely, when the instrument is operated with constant detection efficiency the O^- yield exhibits a series of peaks separated by 0.1 ± 0.01 eV, related to the symmetric stretch vibration in the transient ion. In the present experiment the conditions are somewhere between these two modes and hence the superimposed structures contain contributions from vibrations in the TNI and in the final product CO.

As already shown in the early cluster experiments obtained at poor energy resolution,^{3,4,13,14} electron attachment to CO_2 clusters generates two series of negatively charged ions: (i) non-decomposed complexes of the form $(\text{CO}_2)_n^-$, $n \geq 2$; and (ii) solvated fragment ions of the form $(\text{CO}_2)_n\text{O}^-$, $n \geq 0$. The non-decomposed complexes $(\text{CO}_2)_n^-$ were obviously also generated below the energy of the $^2\Pi_u$ resonance with contributions extending to the range near zero eV. So far, however, no data are available at high energy resolution with the exception of the LPA (laser photoelectron attachment) results mentioned in the Introduction. These ultrahigh energy resolution (1 meV) data cover the very narrow range from threshold to 0.18 eV.

As an example for the formation of a member of the homologous series $(\text{CO}_2)_n^-$, Fig. 2 shows the evolution of the attachment spectrum of the tetramer ion $(\text{CO}_2)_4^-$ with increasing stagnation pressure and hence increasing average size of neutral clusters in the beam. At room temperature and at a stagnation pressure of 3 bar the complex $(\text{CO}_2)_4^-$ is nearly exclusively formed within the threshold region while contributions in the energy range between 1.2 and 4 eV are barely above the detection limit. Only at higher stagnation pressures does the relative intensity of this broad feature increase significantly.

Irrespective of the nature of the associated electronic states (which will be considered below) this behavior can simply be

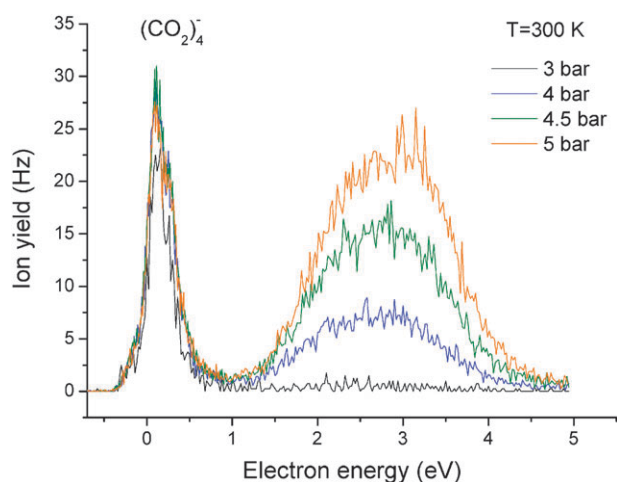


Fig. 2 Evolution of the complex $(\text{CO}_2)_4^-$ as a representative member of the homologous series $(\text{CO}_2)_n^-$ following electron attachment to CO_2 clusters with increasing stagnation pressure and hence increasing average cluster size in the molecular beam (nozzle temperature 300 K).

rationalized from energy arguments. Formation of $(\text{CO}_2)_4^-$ in electron attachment to CO_2 clusters may proceed along the reaction



with $(\text{CO}_2)_n^{-\#}$, the transient cluster anion being formed upon electron attachment. It may then depend on the electron energy whether the excess electron is distributed over the target cluster or whether it becomes localized on a particular molecule thereby forming an individual transient anion which is coupled to the other neutral molecules $((\text{CO}_2)_{n-1}\text{CO}_2^{-\#})$. Tsukada *et al.*¹⁸ suggested that electron attachment to CO_2 clusters leads initially to delocalized states with subsequent quick relaxation into a cluster ion core where the electron is localized. The size of cluster ion core was thereby inferred by Tsukada *et al.*¹⁹ based on their results on photoelectron spectroscopy on $(\text{CO}_2)_n = 2-16^-$. They suggested a C_2O_4^- ion core for $n = 2-5$ and $n = 14-16$ while for $n = 7-13$ the core is CO_2^- . At $n = 6$ both core isomers exist. In view of such an evaporation model the relaxation energy to form $(\text{CO}_2)_4^-$ in its ground state can be used to evaporate the target cluster (formation of $(n-4)$ neutral CO_2 molecules) or to split off the neutral complement of the target cluster $((\text{CO}_2)_{n-4})$. This relaxation energy (or excess energy) is comprised of the energy of the attaching electron plus the *adiabatic* electron affinity of the tetramer cluster. High level *ab initio* calculations predict that the tetramer is at the brink of stability and that the pentamer is the smallest cluster possessing an appreciable positive adiabatic electron affinity.²⁰ Since we can observe a complete series of cluster anions $(\text{CO}_2)_n^-$ with $n \leq 12$, however, with the monomer at much lower intensity than the larger complexes, one is tempted to assume that only the monomer is metastable and cluster ions starting already with the dimer are thermodynamically stable, *i.e.*, all CO_2 clusters possess positive adiabatic electron affinities.

For tetramer anions generated within the narrow resonance at low energy the excess energy is hence very small and one can accordingly assume that the precursor cluster for $(\text{CO}_2)_4^-$ formation is small. This consistently explains the pressure dependence in Fig. 2 indicating that at low stagnation pressures, formation of $(\text{CO}_2)_4^-$ is essentially restricted to the low energy feature. At higher electron energy (between 1.2 eV and 4 eV) the full amount of excess energy (basically the electron energy) has to be distributed and thus target clusters of larger size represent an appropriate medium to generate stabilized $(\text{CO}_2)_4^-$.

Fig. 3 shows that the broad feature in the energy range between 1.5 and 4 eV is a superposition of two resonances with peak maxima at 2.2 eV and 3.1 eV. The relative intensity of these two resonances also depends on the average size of the neutral target cluster in the way that the relative intensity of the 3.1 eV resonance increases with the size of the neutral clusters. In Fig. 3 two spectra are shown recorded at two different nozzle temperatures indicating that the intensity ratio between the higher and lower energy resonance decreases from 1.7 at 300 K to 3.5 at 211 K. This behavior can accordingly be explained by energy arguments: at 3 eV larger clusters represent a more appropriate medium to distribute the larger amount of excess energy.

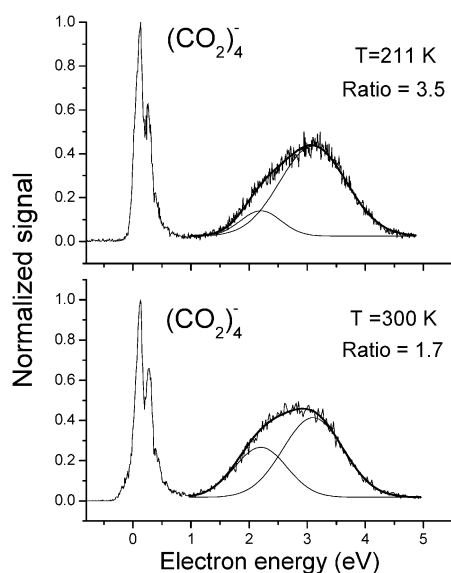


Fig. 3 Deconvolution of the broad contribution between 1 and 4 eV into two resonances peaking at 2.2 and at 3.2 eV. The relative contribution of the 3.2 eV resonance increases with increasing cluster size, *i.e.* decreasing nozzle temperature (upper panel: stagnation pressure 3 bar; lower panel: stagnation pressure 5 bar).

We shall now consider the nature of the resonances involved in the formation of the complexes $(\text{CO}_2)_n^-$. The low energy contribution is apparently associated with the vibrational Feshbach resonances (VFRs) observed in the recent high resolution attachment studies to CO_2 clusters.¹⁵ It was found that the formation of $(\text{CO}_2)_n^-$ ($n = 4-22$) in the energy range between threshold and 0.18 eV is largely mediated through vibrational VFRs of the type $[(\text{CO}_2)_{n-1}\text{CO}_2(\nu_i)]^-$ associated with intramolecular excitations $(\nu_1 \nu_2 \nu_3) = (010)$, $(020)/(100)$ and $(030)/(110)$. These VFRs appear as narrow peaks, *e.g.*, on $(\text{CO}_2)_4^-$ at 62 meV (010) and at 143/155 meV ((100)/(020)), subjected to a red-shift with increasing cluster ion size (amounting to about 120 meV for the double peak (020)/(100) on the $(\text{CO}_2)_{16}^-$ ion).¹⁵ This shift is caused by the increasing binding energy for the diffuse excess electron which is weakly bound by long range forces (solvation effect). The present energy resolution is not sufficient to resolve these VFRs completely but a closer inspection of the low energy domain also reveals structures which are shifted to lower energy with increasing size of the complex $(\text{CO}_2)_n^-$. Fig. 4 indicates clear structures on the tetramer ion $(\text{CO}_2)_4^-$ at 40 meV, 140 meV, 290 meV, 410 meV and 560 meV which we assign to VFRs associated with the excitations (010), (020)/(100), (001), (101)/(021) and (002), respectively, the latter not covered by the ultrahigh resolution laser experiment on the tetramer.¹⁵ On the ion $(\text{CO}_2)_{10}^-$ the visible (020)/(100), (001), and (101)/(021) structures are shifted to 30 meV, 170 meV and 310 meV, respectively, caused by the solvation effect described before.

We propose that the component in $(\text{CO}_2)_4^-$ formation which peaks at 3.1 eV and extends to more than 4 eV is associated with the $^2\Pi_u$ shape resonance. In isolated CO_2 this resonance extends from 2.8 to 4.6 eV and is centered at 3.7 eV as observed in ETS.^{5,6} One can expect that this resonance is subjected to some red shift when bound within the cluster

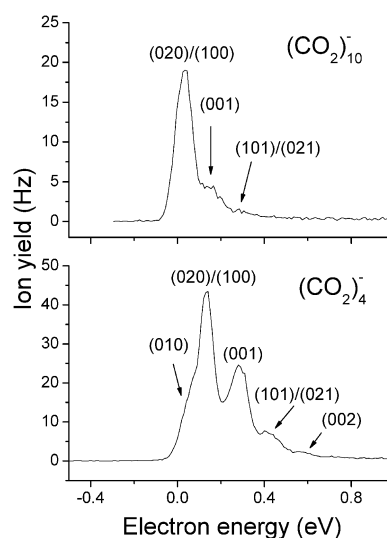


Fig. 4 Formation of the complexes $(\text{CO}_2)_n^-$ in the threshold region. The structures are due to vibrational Feshbach resonances (upper panel: stagnation pressure 2.5 bar, nozzle temperature 220 K; lower panel: stagnation pressure 4.5 bar, nozzle temperature 300 K).

which explains the present peak position at 3.1 eV in $(\text{CO}_2)_4^-$ formation. At the higher energy tail of the $^2\Pi_u$ resonance, DEA becomes energetically available and some of the ion intensity is channeled into products of the form $(\text{CO}_2)_n\text{O}^-$, $n \geq 0$ (see below).

We propose that the resonance located at 2.2 eV is associated with the feature observed in the excitation function of the upper member of the Fermi dyad.⁹ In a single CO_2 low energy scattering leads to a selective excitation of an *in phase* stretching and bending motion with a large amplitude making the neutral molecule either stretched and bent or squeezed and linear. This excitation function exhibits a peak close to zero eV and at 3.5 eV (at the energy of the $^2\Pi_u$ resonance) but also a remarkable intensity in the energy range between 1.5 and 2.5 eV. It thus appears that this resonant scattering process observed in single molecules adds to the formation of anions of the homologous series $(\text{CO}_2)_n^-$ in electron attachment to CO_2 clusters.

Fig. 5 displays formation of the monomer anion CO_2^- which is formed at a comparatively weak intensity. As considered in the Introduction, the monomer anion is most likely metastable with respect to emission of the extra electron. However, when generated in its bent equilibrium geometry, its lifetime ($\approx 60-90 \mu\text{s}^{21}$) is sufficient to be detected by mass spectrometry. CO_2^- has been produced in charge transfer with potassium atoms and in DEA to molecules containing bent CO_2 substructures.²² When generated from CO_2 clusters it is predominantly formed at low energy with some additional small and diffuse contributions in the energy range above 3 eV. From *ab initio* calculations of the potential energy surface of the anion and neutral CO_2 one can conclude that the lifetime of CO_2^- dramatically decreases upon vibrational excitation.¹ We can hence assume that only CO_2^- ions in their vibrational ground state will be detected in the mass spectrometer. From the energetic point of view, only attachment at low energy

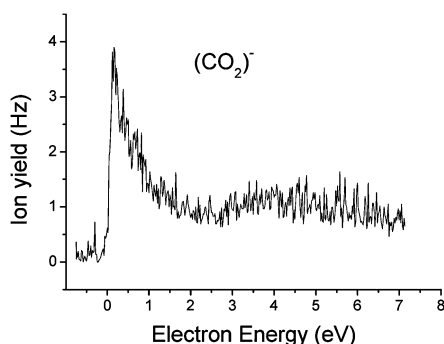
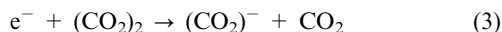


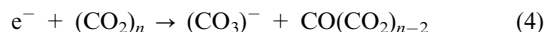
Fig. 5 Formation of the monomer anion CO_2^- following electron attachment to CO_2 clusters. CO_2^- is most likely metastable with respect to emission of the extra electron (stagnation pressure 2.5 bar, nozzle temperature 220 K).

electrons to small clusters will provide favorable conditions, such as attachment to the dimer, *viz.*,

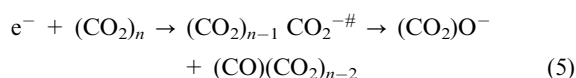


The energetic threshold for this reaction is given by the binding energy of the dimer minus the electron affinity of CO_2 which is most likely negative. From a mechanistic point of view, the low energy electron attached to the dimer must trigger forces which drive the anion in its bent geometry accompanied by a synchronous dissociation of the ion–molecule complex.

Fig. 6 finally presents the lowest member of the series of ion–molecule complexes $(\text{CO}_2)_n\text{O}^-$ ($n = 1$). It has been speculated whether $(\text{CO}_2)\text{O}^-$ is the planar carbonitrioxide radical anion CO_3^- ,⁴ which is known as a stable compound that plays a significant role in the negative ion chemistry of ionized mixtures containing O_2 and CO_2 ²³ and also in the chemistry of the Earth's atmosphere.²⁴ With the standard heat of formation of this anion radical ($\Delta H_f^\circ(\text{CO}_3^-) = -490 \pm 40 \text{ kJ mol}^{-1}$)¹² and the established heats of formation of CO_2 ($-393.5 \text{ kJ mol}^{-1}$) and CO ($-110.5 \text{ kJ mol}^{-1}$) the thermodynamic threshold for the reaction



can be estimated as $\approx 2 \pm 0.5 \text{ eV}$ which is significantly below the experimental appearance energy of this anion ($\approx 3.2 \text{ eV}$). While one cannot completely rule out such a reaction, the more likely scenario is DEA to an individual molecule within the target cluster generating O^- which is liberated from the target cluster either separately or with one or more CO_2 units attached according to the reaction



The ion yield curve in fact resembles that from O^- from isolated CO_2 (Fig. 1) with the difference that the relative contribution from the $^2\Pi_u$ resonance is significantly higher with some shift to lower energy. This red shift is caused by the lowering of the asymptotic energy. The threshold for reaction (5) is given by the gas phase DEA process (4.0 eV, see above)

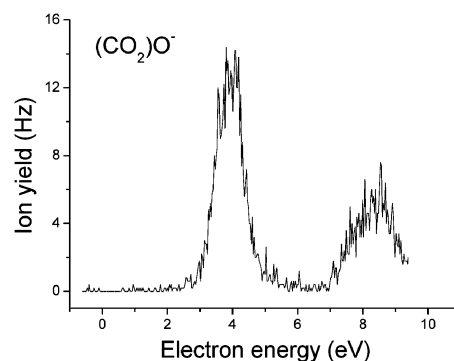


Fig. 6 Formation of the complex $(\text{CO}_2)\text{O}^-$ as a representative member of the series $(\text{CO}_2)_n\text{O}^-$ following electron attachment to CO_2 clusters (stagnation pressure 2.5 bar, nozzle temperature 220 K).

minus the binding energy of the ion–molecule complex $(\text{CO}_2)\text{O}^-$ which may amount to some tenths of an eV.

In summary from the results presented here it can be seen that negative ion formation changes substantially on going from isolated to CO_2 clusters. While in single CO_2 only O^- is generated *via* DEA involving the $^2\Pi_u$ shape resonance at 4.4 eV and a core excited resonance at 8.2 eV, electron attachment to clusters leads to the homologous series $(\text{CO}_2)_n^-$ and $(\text{CO}_2)_n\text{O}^-$. Formation of members of the series $(\text{CO}_2)_n\text{O}^-$ can be interpreted as DEA *via* the $^2\Pi_u$ shape and the core excited resonance involving an individual molecule in the cluster. In contrast, the non decomposed complexes are formed *via* new resonant features, one near threshold (0 eV) and a broad contribution between 1.5 and 4 eV composed of two resonances located at 2.2 eV and 3.1 eV for $(\text{CO}_2)_4^-$. A *virtual state* near zero eV was already introduced in early electron scattering work from single CO_2 ⁷ to describe excitation of the infrared inactive symmetric stretch vibration in the threshold region. Electron attachment to CO_2 clusters in the threshold region is associated with vibrational Feshbach resonances (VFRs), *i.e.* a vibrational excited ion bound to the cluster $(\text{CO}_2)_{n-1}\text{CO}_2(\nu_i)^-$. These VFRs have been discovered and identified in ultra high resolution laser photoelectron attachment studies.¹⁶ Vibrational structure on the $(\text{CO}_2)_n^-$ ion yields in the threshold region are also observed in the present experiment. The 3.1 eV feature leading to the complexes $(\text{CO}_2)_n^-$ can be interpreted as electron capture *via* the lower energy tail of the $^2\Pi_u$ resonance and subsequent intracluster relaxation (evaporative attachment). The 2.2 eV contribution finally is associated with a resonant scattering feature recently discovered⁹ in the selective excitation of the higher member of the Fermi dyad in CO_2 .

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