

Dissociative Electron Attachment to Carbon Dioxide via the 8.2 eV Feshbach resonance

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Momentum imaging experiments on dissociative electron attachment (DEA) to CO₂ are combined with the results of *ab initio* calculations to provide a detailed and consistent picture of the dissociation dynamics through the 8.2 eV resonance, which is the major channel for DEA in CO₂. The present study resolves several puzzling misconceptions about this system.

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Negative ion resonances are ubiquitous in low-energy electron-molecule collisions and provide an efficient vehicle for the transfer of electronic energy to nuclear motion either through vibrational excitation or dissociative electron attachment, the latter process resulting in the formation of both charged and neutral fragments. Recent dynamical studies [1] have shown that DEA to fundamental polyatomic systems can exhibit complex electronic and nuclear dynamics involving symmetry breaking target deformations [2] and, in some cases, conical intersections [3, 4]. Mechanistic studies of the DEA process may give insight into their behavior in the condensed phase [5] and in biological environments [6].

Carbon dioxide offers an interesting case in point. The inverse of DEA to CO₂, i.e. associative detachment, is thought to be important in the catalytic oxidation of CO on a metal surface [7]. In light of its fundamental importance to the understanding of such processes, it is noteworthy that the electronic structure of CO₂ and its metastable anions has not been completely characterized. Most of the extant literature on low-energy electron-CO₂ scattering deals with the short-lived ²Π_u shape resonance near 4 eV, which provides the dominant mechanism for vibrational excitation, while experimental studies of DEA to CO₂ [8–14] have focused mainly on total cross sections and their dependence on electron energy and ion kinetic energy release. The ²Π_u resonance also feeds the CO(¹Σ⁺) + O[−](²P) DEA channel whose thermodynamic threshold lies at 3.99 eV. Scattering calculations [15] show that the ²Π_u resonance becomes sharper and finally electronically bound as the CO bonds are increased along the symmetric stretching coordinate. It is also known that the CO₂[−] ion becomes stable upon bending. It was a long-held belief [16–18] that one component (²A₁) of the ²Π_u resonance, which splits into ²A₁ and ²B₁ components upon bending, correlates with the stable anion, but as Sommerfeld *et al.* [19] have shown, this is not the case. The stable anion correlates with a second, lower energy ²A₁ state which, in linear geometry, becomes a virtual state that dominates electron scattering below 1 eV [20].

By symmetry, there are only three electronic states that can correlate to the CO(¹Σ⁺) + O[−](²P) asymptote. One of these is the ²A₁ state that, in linear geometry, becomes the virtual state. If, as is commonly believed [5, 21], the ²Π_u resonance accounts for the other two states, then we are led to the puzzle whose resolution is a subject of this Letter. The dominant DEA channel in CO₂ is observed at 8.2 eV. Since this energy is less than the 10.0 eV required to produce electronically excited CO* + O[−], the 8.2 eV resonance must necessarily result in electronic ground-state products. So how is this possible when, according to current thinking, all three states arising from this asymptote have already been accounted for? The early theoretical work of Claydon *et al.* [21] and England *et al.* [22] assigned the 8.2 eV peak to a ²Σ_g⁺ shape resonance. This assignment has since been disputed. Srivastava and Orient [13], having found little or no dependence of the 8.2 eV DEA peak on vibrational excitation of the target, suggested it was a Feshbach resonance, citing unpublished theoretical work by Winter supporting their conclusion. Dressler and Allan [14] and, more recently, Huels *et al.* [5] reached a similar conclusion, although there is no consensus about the symmetry of the Feshbach state nor its parent target state and the question of how such a state could feed ground-state products was never addressed.

Our experimental setup, consisting of a momentum spectrometer and an ion detection scheme similar to that used in cold target recoil ion momentum spectroscopy (COLTRIMS) [23], is the same one used in our earlier study of DEA to water [1] and so will not be described in detail here. A stainless steel capillary was used to produce an effusive jet of CO₂ molecules which was crossed at 90° with a pulsed electron beam. The absolute electron energy was determined and checked periodically by measuring the thermodynamic threshold for O[−] production from CO₂, while the momentum spectrometer was calibrated against the well-known O[−] momentum distribution from DEA to O₂. The ion kinetic energy and angular resolution were limited by thermal broadening of the effusive target beam which increases with the square

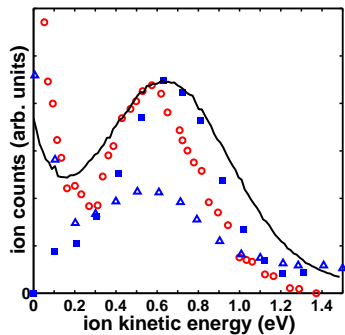


FIG. 1: (Color online) Measured O^- kinetic energy distribution for an incident electron energy of 8.1 eV (solid curve). The experimental data of Chantry [10] (circles) and the uncorrected (triangles) and corrected (squares) data of Dressler and Allan [14] are shown for comparison.

root of the mean kinetic energy[24]. For the present measurements we estimate the overall kinetic energy resolution to be 0.2 eV FWHM, for a mean O^- kinetic energy of 0.7 eV, while the overall angular resolution at this energy was estimated to be 40° FWHM.

The kinetic energy distribution of O^- , for electron attachment energy just below the resonance peak of 8.2 eV, is displayed in Fig. 1, along with previous experimental data found in the literature. The present measurements and the data of Chantry [10] were normalized to the 8.3 eV electron energy corrected data of Dressler and Allan [14] at the 0.6 eV O^- kinetic energy peak, while the uncorrected measurements (triangles in Fig. 1) of the latter work have been maintained on the same scale as their corrected data. The kinetic energy distribution measured by Dressler and Allan depended on the transmission function of their spectrometer, which decreased like $1/E_k$ with increasing ion kinetic energy E_k . They attempted to remove this dependence by weighting the distribution with E_k . Qualitatively, the present data lie between their corrected and uncorrected data, indicating that their correction was somewhat overestimated. The distribution of the present data consists of two peaks, the larger peak having a maximum at 0.6 eV and the smaller one peaking at 0.0 eV. Such a two-peaked structure was calculated for the CO_2^- ($^2\Sigma_g^+$) potential energy surface by Sizun and Goursaud [25], but as stated above, more recent evidence [5, 13, 14] suggest that the $^2\Sigma_g^+$ state is not responsible for the 8.2 eV resonance and that the correct assignment is a doubly excited (Feshbach) state. Since 2-body breakup is the only open channel at these energies, we can determine the kinetic energy distribution of the neutral fragment and its occupied vibrational states directly from the ion kinetic energy distribution using conservation of energy. The nominal electron beam energy is 8.1 eV, which leaves 4.05 eV of excess energy above the thermodynamic threshold, which is the differ-

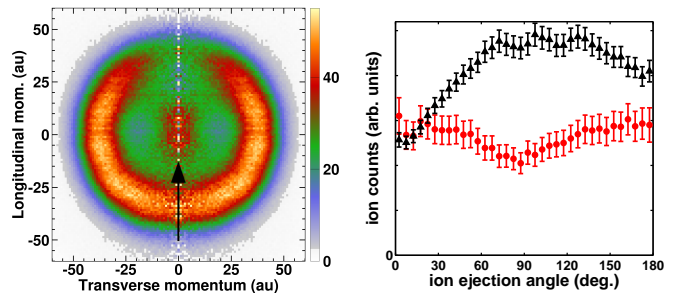


FIG. 2: (Color online) Left: laboratory-frame O^- momentum distribution from DEA to CO_2 for a incident electron energy of 8.1 eV. The arrow indicates the incident electron direction and the intensity scale is the ion yield in arbitrary units. Right: Laboratory-frame O^- angular distribution, with respect to the electron beam direction (0°), for the low-energy (circles) and high-energy (triangles) peaks in the O^- kinetic energy distribution. Error bars represent an estimate of the statistical uncertainty.

ence between the $CO + O$ dissociation energy and the electron affinity of O [24]. The small peak with zero kinetic energy release is a result of dissociation leading to highly vibrationally excited ($\nu = 16$) $CO(X^1\Sigma^+)$ fragments. The main peak spanning O^- kinetic energies of 0.4 eV to 1.1 eV corresponds to a total kinetic energy release, shared between the two fragments, of 0.6 eV and 1.7 eV, which implies population of mostly the $\nu = 9$ to $\nu = 13$ vibrational levels of the CO ground state.

To investigate the origin of the main peak in the O^- kinetic energy distribution, we examine the ion momentum and angular distributions with respect to the electron beam direction. The momentum distribution, displayed in the left panel of Fig. 2, shows an asymmetric angular distribution, peaking at wide backward angles with respect to the electron beam direction. Ion angular distributions for each of the two peaks in the kinetic energy distribution are displayed in the right panel Fig. 2, where we have integrated over two subsets of the ion kinetic energy in order to separate the two distributions. The low-kinetic energy angular distribution tends to considerably wider angles than the main kinetic energy peak, which is consistent with the slower ions following very different trajectories compared to the faster ions.

To assist with the interpretation of the measured data, we carried out both *ab initio* electronic structure and fixed-nuclei electron scattering calculations. Neutral CO_2 is a linear closed-shell molecule nominally described, near its equilibrium geometry, by the electronic configuration $(core)^{12} (\sigma_g)^2 (\sigma_u)^2 (\pi_g)^4 (\pi_g)^4$. The neutral target states were described by complete-active-space (CAS) configuration-interaction (CI) calculations with state-averaged multi-configuration-self-consistent-field (MCSCF) orbitals, in which we doubly occupied the first five orbitals, and included an additional π^* and a Rydberg σ^* orbital in the active space. The negative

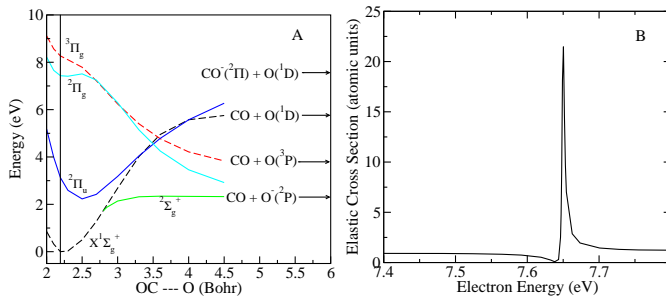


FIG. 3: (Color online) Left: collinear potential energy curves for CO₂ (dashed) and CO₂⁻ (solid). One CO distance is fixed at 2.195 bohr. Vertical line indicates equilibrium geometry. Right: ²Π_g component of e⁻ - CO₂ elastic cross section at equilibrium geometry.

ion states were then obtained by carrying out multi-reference CI calculations consisting of a CAS CI + all single-excitations into virtual orbitals. Such a treatment attempts to strike a balanced description of correlation in the neutral and negative ion states, although it is admittedly biased toward the anion states. The results of these calculations are summarized in Fig. 3a, which shows a cut through the potential energy surfaces in linear geometry where one CO distance is fixed and the other varied. In plotting the results, the anion states were all shifted upward by 0.7 eV relative to the neutral ground state, said shift chosen to make the ²Σ⁺ virtual state coincide with the neutral ground state in the region where the former is unbound. In addition to the ²Π_u anion, we find a doubly excited ($\pi_g^3\sigma^{*2}$), ²Π_g negative ion state, whose parent is the ³Π_g excited state of the neutral target. We note that near the equilibrium geometry of the neutral, the ²Π_g state lies below all the electronically excited CO₂ states and can thus only autodetach into the e⁻ + CO₂ (X¹Σ_g⁺) continuum. The surprising result is that it is the ²Π Feshbach state, along with the ²Σ⁺ virtual state, that correlate with CO(¹Σ⁺) + O(²P) in linear geometry. There is a sharp avoided crossing between the ²Π shape resonance and the ²Π doubly excited state in linear geometry, the former correlating with a short-lived CO⁻, ²Π anion + O (¹D). There is in fact a conical intersection between the ²Π states close to the point where they avoid in linear geometry.

To further characterize the doubly excited state, we carried out fixed-nuclei complex Kohn scattering calculations with the same prescriptions for constructing the N-electron target states and N+1-electron scattering states that were employed in the structure calculations. Figure 3b shows the ²Π_g component of the elastic cross section at equilibrium geometry near the resonance energy. A Breit-Wigner fit to the results confirmed the resonance to be extremely long-lived, with a width of ~0.004 eV. We must emphasize that these results are for a single geometry. When convoluted over vibrationally weighted

geometries in the Franck-Condon region, no sharp features would be expected to be seen in the elastic cross section, which explains why the observed 8.2 eV DEA peak is not visible in the transmission spectrum [14].

To connect the theoretical results to the observed laboratory-frame angular distributions, we calculate the entrance amplitude, formally defined as $V(\theta, \phi; \mathbf{S}) = \langle \Psi_{bg}^+(\theta, \phi; \mathbf{S}) | H_{el} | \Psi_{res}(\mathbf{S}) \rangle$, where Ψ_{bg}^+ is a background scattering function with a plane-wave incident on the target in the direction θ, ϕ , Ψ_{res} is the resonance wavefunction, H_{el} is the electronic part of the Hamiltonian and \mathbf{S} labels the internal coordinates of the molecule. The electron attachment probability, a function of θ and ϕ expressed relative to the dissociation axis in the molecular frame, is computed from the squared modulus of the entrance amplitude. In practice, we can evaluate the entrance amplitude in terms of quantities obtained from an analysis of the calculated fixed-nuclei S-matrix, as outlined in ref. [26]. The attachment probability can be directly related to a laboratory frame angular distribution when the axial recoil condition is met, requiring in the present case that the recoil axis which connects the atom ion and the diatom center of mass does not rotate during the dissociation. Under these assumptions, the laboratory angular distribution is obtained by averaging the attachment probability over initial and final target rotational states, which eliminates its dependence on ϕ .

Since asymmetry is clearly observed in the angular distributions, it is important to incorporate the effects of zero-point bending and asymmetric stretch motion into the calculation of the entrance amplitudes. In order to simplify the calculations while gauging the importance of these effects, we obtained the entrance amplitudes from scattering calculations with the nuclei located at their root-mean square (RMS) values, assuming harmonic asymmetric stretch and bending potentials. Figure 4 shows the calculated entrance amplitudes and angular distributions at both the equilibrium and RMS geometries. While the angular distribution computed at the RMS geometries gives results in better agreement with experiment than the equilibrium geometry result, the magnitude of the observed asymmetry clearly implies that there must be post-attachment bending involved in the dissociation dynamics. To show this effect, the right-most panel of Fig. 4 shows results (labelled ‘convolved’) in which the angular distribution is calculated by adding 3 degrees to the axial recoil angle and convolving the computed values with a 55° FWHM Gaussian distribution to simulate the finite resolution of the experiment. The agreement with the experimental distribution at 0.7eV O⁻ KE is quite good. These results indicate that it is likely that the electron attaches preferentially on the stretched side of the molecule and subsequent dynamics tends to favor dissociation in linear geometry.

The present results provide new insight into the topol-

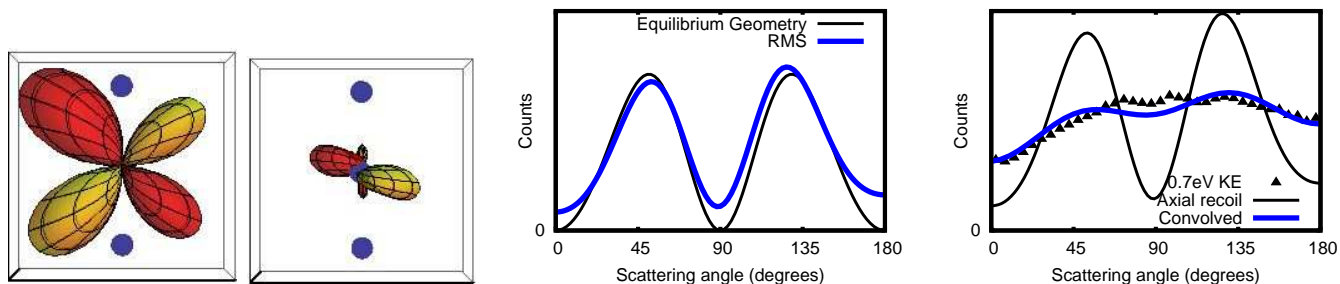


FIG. 4: (Color online) Entrance amplitudes and angular distributions for CO₂ DEA through the ²Π Feshbach resonance. Left to right: real and imaginary parts of the entrance amplitude calculated at RMS values of bend and asymmetric stretch; calculated O⁻ angular distributions at equilibrium and RMS geometries; comparison of calculated and measured angular distributions (see text).

ogy of the CO₂⁻ anion states and the dynamics of dissociative attachment in this system. This study again illustrates that, even with small polyatomic targets, an understanding of anion dissociation dynamics beyond simple one-dimensional models can be crucial in interpreting measured data. By combining the results of momentum imaging spectroscopy with *ab initio* theory we are able to clearly show that the 8.2 eV DEA peak in CO₂ is initiated by electron attachment to a dissociative, doubly excited ²Π state that interacts with a lower ²Π shape resonance through a conical intersection and dissociates to electronic ground-state products. Mapping out the conical intersection(s) is complicated since bending breaks the degeneracy of the ²Π states, resulting in a pair of A' and A'' states with different topologies. This topology, and the role it plays in understanding DEA through the 4 eV shape resonance, will be the subject of a longer paper.

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