We present a combined experimental and theoretical study for electron-impact ionization of carbon dioxide ($\text{CO}_2$) for the projectile energy $E_0 = 100$ eV. Experimental triple-differential cross sections (TDCS) are obtained using a multi-particle momentum spectrometer (reaction microscope). For projectile scattering angles between $-5^\circ$ and $-20^\circ$ a large part of the full solid angle is covered for the slow ejected electron with energies between 5 and 15 eV. The experimental data are measured for the ionization of the three outer valence molecular orbitals $1\pi_g$, $1\pi_u$, and $3\sigma_u$ which lead to a non-dissociating $\text{CO}_2^+$ ion. The measured TDCS summed over all three orbitals are internormalized across the scattering angles and ejected electron energies. They are compared to the theoretical results from the multi-center distorted wave (MCDW) approximation, and from the MCDW-WM approximation which includes post-collision interaction using the Ward–Macek factor (WM). Reasonable good agreement is found between the experiment and the MCDW-WM calculations for the angular dependence and the relative magnitude of the cross sections in the coplanar plane, while for the perpendicular and full perpendicular planes larger discrepancies exist. Since post-collision interaction is not considered the MCDW method shows strong discrepancies with experiment for small mutual angles of the two outgoing electrons in the final state.
fixed by energy conservation. Such experiments serve as a powerful tool to comprehensively test theoretical models [5–7]. Earlier experiments could measure one particular kinematics at a time like electron emission within the projectile scattering plane with fixed energies of the outgoing final state electrons. In recent years, experimental techniques were developed that allow to simultaneously access a large fraction of the entire solid angle and a large range of energies of the continuum electrons in the final state and, thus, TDCS in three dimensional (3D) representations were obtained [8, 9]. In the same time theory has made tremendous progress in describing the electron-impact ionization dynamics of the simplest targets. The fundamental atoms hydrogen and helium are now considered to be well understood [10–14]. More recently sophisticated methods were also demonstrated for Ne(2p) and Ar(3p) [15–17].

For molecules electron-impact ionization of the fundamental H2 molecule was mostly studied in experiments and several successful theoretical models were developed which can reproduce the observed electron emission patterns even within the molecular frame, i.e., for fixed-in-space molecular axis (see, e.g., [18–22]). Studies concerning the ionization dynamics of larger and more complex molecules, however, are less numerous. The agreement between theories and experiments is not as good as for the simpler targets; see, e.g., [23–30]. One of the reasons is the multi-center structure of molecules which is not straight forward to include in theoretical models in all its aspects. Here, we studied the ionization dynamics of carbon dioxide (CO2) which is a triatomic linear molecule and plays important roles in nature and in technical applications. CO2 is relevant in research fields from astrophysics to radiation chemistry, and it is the main component in the atmospheres of Venus and Mars. In the laboratory work, CO2 is widely used in various discharges, plasmas, laser systems and more.

For electron-impact ionization of CO2 there exist only a few measurements for particular kinematical conditions—all restricted to the so-called coplanar geometry in which the incoming electron and both final-state electrons move in one common plane [27, 28, 31]. Lahmam-Bennani et al [27] have measured two kinematics for relatively high impact energy E = 500 eV, 6° scattering angle and two ejected electron energies of 37 and 74 eV. They studied the two cross section maxima which are characteristic for (e, 2e) reactions namely the maximum directed along the projectile momentum transfer direction (the binary peak) and the second maximum along the reversed direction (the recoil peak). Comparison with theoretical results using the first Born approximation—two-center continuum (FBA-TCC) approach showed rather poor agreement concerning the width of the binary peak and the relative intensity of the recoil peak. More recently the TCC approach was refined to three target centers (ThCC) [29] which should be more appropriate for the three-atomic CO2 molecule. Additionally, the authors have extended the basis for representing the target wave functions such that the binary peak agreement could be improved. More recently, Ozer et al published coplanar TDCS for an intermediate projectile energy of 250 eV, 37 eV ejected electron energy and three different projectile scattering angles [28]. These were compared to the ThCC approximation which again did not well describe the binary peak structure and width as well as the recoil peak intensity. Here the molecular three-body distorted wave (M3DW) theory was clearly in better agreement although some discrepancies still exist between M3DW results and experiment.

The earliest (e, 2e) study on the CO2 ionization dynamics was performed by Hussey and Murray [31]. They performed measurements at low impact energy from around 24–100 eV at coplanar symmetric geometry where both outgoing electrons have the same energies and symmetrically equal angles. So far no theoretical calculations were published for this fairly challenging kinematics.

A theoretical model, which has been frequently used to describe the ionization dynamics in complex molecules, is the sophisticated M3DW method which uses orientation-averaged molecular orbitals (OAMO) [7]. Recent (e, 2e) studies of CH4 and H2O indicate that it is more accurate to perform a proper average (PA) over orientation-dependent cross sections rather than to use the OAMO for calculations [32, 33]. The computational cost of the PA method, however, is much higher than the OAMO. Finally, a multicenter distorted wave (MCDW) method has been developed recently to describe the ionization dynamics of molecules. So far, the MCDW method has been tested with TDCS in the coplanar geometry. Good agreement between MCDW and experiment is obtained for (e, 2e) on CH4 and the formic acid (HCOOH) molecules [34, 35]. Therefore, in the present work we examine if this theoretical approach yields proper results for CO2 as well.

Here, we performed a kinematically complete study for electron-impact ionization of CO2 at the relatively low energy E0 = 100 eV and strongly asymmetric energy sharing of the outgoing electrons. The measured TDCS are covering a large part of the full solid angle for the slow emitted electron. In this energy regime, the ionization dynamics becomes more sensitive to the multi-center potential of the molecule and physical effects such as post-collision interaction (PCI) and, e.g., charge-cloud polarization in the projectile-target interaction, and so accurate modelling of the ionization process is challenging. The experimental data in this work, therefore, would provide a good basis for thoroughly testing theoretical models. Ionization of the 1πg, 1πu, and 3σu orbitals is observed where we do not energetically resolve the individual states. The resulting parent ions are stable and do not dissociate:

\[ e_0(E_0) + CO_2 \rightarrow CO_2^+ + e_1(E_1, \theta_1) + e_2(E_2, \theta_2, \phi_2). \]  (1)

Here \( e_0, e_1 \) and \( e_2 \) are the incoming projectile, a faster (scattered) electron with energy \( E_1 \) and a slower (ejected) electron with energy \( E_2 \), respectively. The angle of the scattered electron with respect to the incoming beam axis is \( \theta_1 \). The respective ejected electron angle is \( \theta_2 \) and its angle out of the scattering plane which is defined by the incoming and scattered projectile is \( \phi_2 \). Since the experimental data are internormalized for all different kinematical situations, a single common scaling factor is sufficient to fix the absolute value of all the experimental data which then can be compared with the theoretical
calculations. The results presented here cover three ejected-electron energies \((E_2 = 5, 8 \text{ and } 15 \text{ eV})\) and four projectile scattering angles \((\theta_p = -5^\circ, -10^\circ, -15^\circ, -20^\circ)\).

The experimental results of TDCS are compared to the above mentioned MCDW method. The MCDW prediction is developed within the framework of the FBA in which a plane wave is used to describe the incoming and scattered projectile. The multicenter nature of the molecule is treated by describing the slow ejected electron by a distorted wave moving in the multicenter potential. This method does not include the PCI between two outgoing electrons. PCI is accounted for in the MCDW-WM model with the Gamow factor calculated within the Ward–Macek (WM) approximation [36].

This paper is structured as follows. We give a brief description of the experimental method in section 2. A short note on theoretical model is presented in section 3. The results are discussed in section 4. Finally, the conclusions of this study are given in section 5.

2. Experimental method

The experiment has been performed using an advanced reaction microscope which was designed especially for electron-impact ionization studies. Detailed information on this apparatus was given elsewhere [8, 13, 37]. Here, we give a brief description of the experimental procedure. A pulsed electron beam from a thermo-cathode is crossed with a cold target in form of a supersonic molecular jet. The carbon dioxide gas expands from a stagnation pressure of 2 bars through a nozzle of 30 \(\mu\)m diameter into a vacuum chamber \((10^{-3} \text{ mbar})\). It passes two skimmers for collimation and differential pumping and enters the main scattering chamber with \(10^{-8} \text{ mbar}\) pressure.

The negative electrons as well as the positive recoil ion produced in ionizing collisions are extracted by homogeneous electric and magnetic fields into opposite directions and projected on two position- and time-sensitive detectors. In this experiment an \((e, 2e + \text{ion})\) measurement was performed, i.e., triple-coincidences of both outgoing electrons and the \(\text{CO}_2^+\) cation were recorded. From the positions of the hits on the detectors and the times-of-flight, the vector momenta of the particles can be calculated. It should be noted that the projectile beam axis (defining the longitudinal direction and the \(z\)-axis) is adjusted exactly parallel to the electric and magnetic extraction fields. As a result, after passing the target gas jet the projectile beam reaches the center of the electron detector where a central bore in the micro-channel plates allows the beam to pass without inducing a signal. With this setup a large part of the full solid angle is covered, 100\% for the recoil ions and about 80\% for secondary electrons below \(E_2 = 15 \text{ eV}\). Due to the detector hole there is a blind angular range for electrons with small forward and backward emission angles which depends on the electron energy. In addition secondary electrons which undergo an integer number of cyclotron revolutions in the magnetic field end up in the detector hole. As result experimental runs with three different electrical extraction fields were performed in order to maximize the accessible angular range. For the three electron energies \(E_2\) analyzed the following angular ranges are covered. \(E_2 = 5 \text{ eV}; \theta_p = 25^\circ–145^\circ\) and \(215^\circ–335^\circ, E_2 = 8 \text{ eV}; \theta_p = 35^\circ–155^\circ\) and \(205^\circ–325^\circ, E_2 = 15 \text{ eV}; \theta_p = 25^\circ–165^\circ\) and \(195^\circ–335^\circ\).

The coincidence data were accumulated simultaneously for the different scattering angles \(\theta_p\) and ejected electron energies \(E_2\). Therefore, the TDCS which were obtained in the offline data analysis by sorting the events according to projectile scattering angles and ejected-electron energies are internormalized. For the energy calibration of the electron spectrometer, we use the ionization of the neon atom in the \(2p\) orbital which was measured with the same experimental settings.

3. Theoretical models

The MCDW method has been discussed in detail previously [34, 38]. Here we will give only a brief outline. The MCDW model is used to study the electron impact single ionization process for molecules under asymmetric kinematics with special attention on the multicenter continuum wave function of the ejected electron. It is formulated in the framework of the FBA with the incident and scattered electron being described by plane waves. The transition amplitude for a given molecular orientation in the laboratory can be written as:

\[
T^\text{MCDW}_\beta(\Omega) = \langle k_1|\Psi^{(-)}_f(k_2; R_{\Omega}^{-1}|r)\rangle \langle V(|r)|k_0\Psi_f(R_{\Omega}^{-1}|r)\rangle, \tag{2}
\]

where \(k_0, k_1, \) and \(k_2\) represent the momentum vectors of the incident, scattered, and ejected electrons respectively. The molecular orientation is defined by the Euler angle \(\Omega = (\alpha, \beta, \gamma)\). The operator \(R_{\Omega}^{-1}\) represents the rotation of the target. \(|\Psi_f\rangle\) is the initial bound wave function, and \(|r\rangle\) refers to the set of electronic coordinates. In the final state \(|\Psi^{(-)}_f\rangle\) the ionized orbital is substituted by the continuum wave function of the ejected electron. \(V\) is the full interaction potential of incident electron and the molecular target. The incident and scattered electrons are described by plane waves \(|k_0\rangle\) and \(|k_1\rangle\). With the help of the Bethe integral, equation (2) can be simplified as an one electron problem under the frozen core approximation:

\[
T^\text{MCDW}_\beta(\Omega) = \frac{4\pi}{K^2} \langle \mathcal{F}^{(-)}_\beta(k_1; R_{\Omega}^{-1}|r) | e^{iK_r}\rangle - \sum_n Z_n e^{iR_n} \frac{1}{N} |\phi_n(R_{\Omega}^{-1}|r)\rangle, \tag{3}
\]

where \(K = k_0 - k_1\) is the momentum transfer vector. \(R_n\) is the position vector of the \(n\)th nucleus, and \(Z_n\) indicates its charge. Vector \(r\) represents the position of the active electron. \(|\mathcal{F}^{(-)}_\beta\rangle\) is the continuum wave function of the ejected electron, and \(|\phi_n\rangle\) is the bound orbital to be ionized. The first term in equation (3) represents the scattering by the active electron, and the second term refers to the scattering by the nuclei. In the present calculation model, the continuum wave function of ejected electron is solved in the multicenter potential of molecular ion under frozen...
core approximation, and is generally not orthogonal to the bound orbital \(|\phi_k\rangle\). So the second term in equation (3) which represents the nuclear distribution will not disappear and will be fully included.

In the high impact energy regime with projectile energies in the order of keV, the correlation of the two outgoing electrons is weak enough to be ignored. However, under the present low collision energy condition, the PCI must be accounted for. Here it is described by the WM factor [36]:

\[
|C_{21}^{WM}|^2 = \frac{2\pi\eta}{e^{2\pi\eta} - 1} \left| F_1 \left( \eta, 1, -i\frac{r_{save}}{\eta} \right) \right|^2,
\]

where \(\eta = 1/|k_2 - k_3|\). \(F_1\) is the confluent hypergeometric function. \(r_{save}\) is defined as:

\[
r_{save} = \frac{\pi^2}{16(E_2 + E_1)} \left( 1 + \frac{0.627}{\pi} \sqrt{E_2 + E_1} \ln(E_1 + E_2) \right)^2.
\]

(5)

\(E_2\) and \(E_1\) are the corresponding energies of ejected and scattered electrons. With the WM approximation, the T-matrix becomes:

\[
T_{\beta}^{MCDW-\text{WM}}(\Omega) = C_{21}^{WM} T_{\beta}^{MCDW}(\Omega).
\]

(6)

Thus, the transition amplitude is scaled depending on the relative momentum and the energies of the two outgoing electrons. Finally, the TDCS is obtained by averaging over all molecular orientations:

\[
\frac{d^3\sigma}{d\Omega_2 d\Omega_3 dE_1} = |C_{21}^{WM}|^2 \frac{k_2 k_1}{(2\pi)^5 k_0^2} \frac{1}{8\pi^2} \int [T_{\beta}^{MCDW}(\Omega)]^2 d\Omega.
\]

(7)

In order to obtain the multicenter continuum wave function of ejected electron in the potential of molecular ion, a model potential is adopted [38]:

\[
V^m = V^{un} + V^{cp} + V^{\text{model exc}},
\]

(8)

where \(V^{un}\) is the electrostatic potential between the incident electron and residual molecular ion, \(V^{cp}\) is the correlation-polarization potential and \(V^{\text{model exc}}\) is the exchange potential. The Schrödinger equation for the ejected electron is:

\[
\left[ \frac{1}{2} \nabla^2 + V^m - E_k \right] \psi^{(-)} = 0.
\]

(9)

To solve this equation, the single-centered expansion technique [39–41] is employed. The wave function and potential are expanded using the symmetry-adopted angular functions. Note that the model potential \(V^m\) is anisotropic and introduces the coupling between terms of different angular momentum in the partial wave expansion of \(\mathcal{F}^{(-)}\), resulting in a set of coupled equations. As shown in the work [42], the diagonal terms in the potential matrix are considered dominant. Therefore, in the present work the off-diagonal elements were ignored and the decoupled partial wave equations were solved in the practical calculations. This means that coupling between different angular momenta is ignored.

4. The CO₂ target

CO₂ is a linear triatomic molecule and the ground state electronic configuration of this molecule is given by

\[
(1\sigma_u)^2(2\sigma_u)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2 \times (1\pi_u)^2(1\pi_u)^2 X^1\Sigma_g^+.
\]

(10)

The vertical ionization potentials of the three outermost \(1\pi_u\), \(1\mu_u\) and \(3\sigma_u\) orbitals are 13.8 eV, 17.6 eV, and 18.1 eV, respectively [43, 44]. Here we study ionization of an electron from one of these orbitals which will lead to stable non-dissociating CO₂⁺ in the ionic states \(X^1\Pi_g, \Lambda^3\Pi_u\) and \(B^3\Sigma_u^+\), respectively. In the present experiment the \(1\pi_u\), \(1\mu_u\), and \(3\sigma_u\) orbitals are not resolved due to the limited binding energy resolution. Thus, the experimental data represent the summed TDCS for the ionization of these three orbitals. Ionization of other orbitals does not contribute since the residual ion dissociates and does not give rise to a coincidence signal with the parent ion. For the discussion of the TDCS below it is useful to know the characteristics of the momentum profiles of the orbitals. The momentum profile of an orbital is defined as its density function in momentum space, i.e., the square modulus of its wave function in momentum space. The spherically averaged momentum profiles of the CO₂ orbitals have been investigated experimentally and theoretically by Leung and Brion [45]. Figures 2(a)–(c) shows the \(1\pi_u\), \(1\mu_u\), and \(3\sigma_u\) orbitals in position space obtained with the Gaussian 16 quantum-chemistry package [46]. The respective momentum space densities obtained by Fourier transformation of the position space orbitals are shown in the panels (d)–(f). Clearly the three outermost orbitals have \(p\)-character, i.e., their momentum profiles are zero for \(k = 0\) and they have maxima for \(k \neq 0\). The orientation averaged highest occupied molecular orbital (HOMO) \(1\pi_u\) and \(1\mu_u\) (HOMO-1) orbitals have maxima at \(k = 0.8\) a.u. and 0.65 a.u., respectively. The \(3\sigma_u\) (HOMO-2) orbital has two maxima at \(k = 0.5\) a.u. and 1.6 a.u. [45].

In the theoretical TDCS calculation, the equilibrium linear molecular geometry is used with a C–O bond length of 1.163 Å. The wave functions of the molecular orbitals of CO₂ are calculated by the density functional theory method employing B3LYP hybrid functional [47, 48] with cc-pVTZ basis set [49]. If \(l_{\text{max}}\) and \(l'_{\text{max}}\) denote the upper limits of the angular momentum in the partial wave expansions for the bound orbital and continuum wave functions, respectively, the convergence is reached with \(l_{\text{max}} = 10\) and \(l'_{\text{max}} = 18\) in our calculations. In the single-center expansion, \(r\) ranges from 0 to 8.47 a.u. with increasing step size from 0.01 to 0.128 a.u. The convergence of the numerical spherical average is achieved with the Euler angle mesh \(N_{\alpha} = 6, N_{\beta} = 10, N_{\gamma} = 20\), where \(N_{\alpha}, N_{\beta}, \) and \(N_{\gamma}\) represent the number of points for the Euler angles \(\alpha, \beta\), and \(\gamma\), respectively.
5. Results

The FDCS is analyzed for different fixed scattering angles of the outgoing fast electron and over a large range of emission angles of a slow electron. A schematic diagram illustrating the observed kinematic geometries and an exemplarily TDCS is presented in figure 1(a). The projectile with momentum \( k_0 \) enters from the bottom and is scattered to the left with momentum \( k_1 \). These two vectors define the scattering \( xz \)-plane as indicated by the red solid frame in figure 1(a). For asymmetric energy sharing as it is the case in the present study the fast outgoing electron can be safely considered as the scattered projectile and the momentum transferred to the target \( q \) indicated in figure 1(a) is defined as \( q = k_0 - k_1 \). The TDCS is plotted as function of the slow electron emission direction as 3D surface. For a quantitative comparison of the experimental and theoretical results over a large range of the measured phase space we present cuts through the 3D TDCS for three different planes of the low energy electron as indicated in figure 1(a). In the coplanar \( xz \)-plane the slow ejected electron is detected in the scattering plane (red solid frame). The perpendicular \( yz \)-plane contains the incoming beam axis and is perpendicular to the scattering plane (green dotted frame). Finally, the full perpendicular \( xy \)-plane is perpendicular to the incoming projectile beam axis (blue dashed frame).

The TDCS for these three geometries as function of ejected electron emission angle are presented in the figures 3–5. For each geometry particular values for ejected electron energy of \( E_2 = 5, 8 \) and 15 eV and for the projectile scattering angle of \( \theta_1 = -5^\circ, -10^\circ, -15^\circ, -20^\circ \) are chosen. The integration ranges of \( E_2 \) and \( \theta_1 \) are given in the caption of figure 3. Furthermore, the data are integrated over an out-of-plane angular range of \( \pm 10^\circ \). The experimental data are compared to the MCDW and MCDW-WM results. For the MCDW theory not including PCI, the TDCS for the individual orbitals \( 1\pi_g, 1\pi_u \), and \( 3\sigma_u \) as well as their sum are presented in the diagrams.

By multiplying the MCDW data with the WM factor to obtain the MCDW-WM result the cross section is scaled down depending on the mutual emission directions and relative magnitudes of the momenta of both electrons such that PCI is approximated. For normalization of the relative experimental data to the theory the absolute scale of the MCDW theory was considered to be relevant since it is known that inclusion of the WM-factor does not maintain the normalization of the total cross section. On the other hand as will be discussed below and as is visible in figure 3(a) the shape of MCDW-WM is in much better agreement with experiment than MCDW. Therefore, we scaled the MCDW-WM results such that they are in agreement with the MCDW calculation in the vicinity of \( \theta_2 = 180^\circ \) of figure 3(a). Here the difference of both models should be the smallest since both final state electrons are ejected approximately back-to-back and, therefore, PCI is minimal. This scaling factor was 1.73 for all geometries. Then the experimental data for the scattering plane and \( \theta_1 = -5^\circ, E_2 = 5 \) eV were scaled to the MCDW-WM calculation for achieving the best visual fit (figure 3(a)). The same factor was subsequently applied to the experimental data of all other geometries since as mentioned above the experimental data are cross normalized.

Figure 3 presents the TDCS in the \( xz \)-scattering plane, i.e. the coplanar geometry which contains the momentum transfer vector \( q \). Its direction as well as its opposite direction is indicated in the diagrams by the arrows labeled \( +q \) and \( -q \), respectively. It is observed that in the coplanar geometry the TDCS has generally a two-lobe structure. One lobe is oriented roughly along the direction of the momentum transfer \( q \). This lobe is well known as binary lobe and is due to a single binary collision between the projectile electron and the bound target electron. The second (recoil) lobe is found approximately opposite to the momentum transfer direction. Here the outgoing slow electron backscatters in the ionized potential [5, 6]. In order to better understand the shapes and widths of the lobes we consider ionization for the moment as the result of a pure first-order binary collision of the projectile and the target electron and neglect all further interactions in the initial and final states. Then, the ejected electron momentum is simply the sum of its initial momentum in the bound state and the momentum transfer \( q \). Thus, the emission pattern is strongly influenced by the momentum profile of the ionized orbital.
For example, for ionization of orbitals with $p$-character which have a node for zero momentum there will be no ionized electrons observed for the momentum vector $k_2$ being equal to the momentum transfer vector $q$. Thus, for this so-called Bethe Ridge kinematics with $|k_2| = |q|$ a cross section minimum in the binary peak should be found such that the binary peak shows a two-maximum pattern. In table 1 the absolute values $k_2$ and $q$ are listed for all scattering kinematics shown in figures 3–5. We see, e.g., for $E_2 = 15\text{ eV}$ that for small scattering angle $\theta_1$ Bethe Ridge kinematics is not fulfilled and in figure 3(i) the theoretical cross sections for the all the individual orbitals show a single binary peak. For increasing $\theta_1$ Bethe Ridge kinematics is approached and the $p$-character of the orbitals shows up in form of a double-lobe binary peak. In accordance with the positions of the maxima of the different momentum profiles mentioned above and shown in figures 2(d)–(f) the angular separation of the two lobes is largest for the $1\pi_u$ orbital and smaller for the $1\pi_g$ and $3\sigma_u$ orbitals. This is visible in particular for large scattering angle $\theta_1$. For the $3\sigma_u$ orbital there is even an indication of the second higher momentum peak of the momentum profile at $\theta_2 = 130^\circ$ and $330^\circ$. Interestingly these features originating from the orbital momentum profiles become more pronounced if $q$ exceeds $k_2$ as it is the case in panels (h) and (d) of figure 3. On the other hand, at low energy $E_2$ additional distortion effects, e.g., due to the molecular ionic potential become visible in form of a third maximum developing in the middle of the binary peak for the $1\pi_g$ orbital. The recoil peak

is more difficult to understand since in most cases in figure 3 it is a rather structureless single peak except for $1\pi_u$ where for large $q$ there is also an indication of a double peak. The relative recoil lobe magnitudes vary for the three orbitals with generally large intensities for $1\pi_g$ and for $1\pi_u$ and a clear minimum for $3\sigma_u$ as if there is a deconstructive interference of different contributions right at the $-q$ direction. For one case ($\theta_1 = -20^\circ$, $E_2 = 5\text{ eV}$) the 3D MCDW-WM results for the individual orbitals are shown in figures 1(b)–(d). Here, the central maximum in the $1\pi_g$ binary peak is obvious. For $3\sigma_u$ the deep minimum in the binary peak is visible. In addition a secondary structure is visible in form of a torus with its cross section maximum perpendicular to the binary peak minimum.

For the summed TDCS (MCDW sum) some details of the individual orbitals’ TDCS naturally average out as it is the case for the third maximum in the center of the $1\pi_g$ binary

Table 1. The momentum $q$ transferred by the scattered projectile to the target for all values of the projectile scattering angle $\theta_1$ and the ejected electron energy $E_2$ (momentum $k_2$) of figures 3–5.

| $E_2$ (eV) | $k_2$ (a.u.) |
|-----------|-------------|
| 5 \text{ eV} | 0.36 a.u. | 0.40 a.u. | 0.50 a.u. |
| 8 \text{ eV} | 0.53 a.u. | 0.55 a.u. | 0.62 a.u. |
| 15 \text{ eV} | 0.73 a.u. | 0.74 a.u. | 0.79 a.u. |

Figure 2. The CO$_2$ $1\pi_g$ (a), $1\pi_u$ (b), and $3\sigma_u$ (c) orbitals in position space. The central sphere is the carbon atom, the two spheres on either side are the oxygen atoms. (d), (e) and (f) are the respective momentum space densities.
lobe and the maxima at 130° and 330° of the 3σ_u TDCS (see, e.g., figures 3(c), (d)). Nevertheless, the one/two lobe pattern of the binary peak and partly also of the recoil peak (see figure 3(d)) is retrieved. Inclusion of PCI strongly modifies the emission pattern as can be seen in going from the MCDW-sum to the MCDW-WM results. PCI is particularly strong for small momentum differences of both outgoing electrons, i.e., for small relative emission angles and more symmetric energy sharing. Therefore, the PCI-induced suppression of the binary peak is reduced for increasing projectile scattering angle θ. This is seen by going from the diagrams of the first row in figure 3 to the last row since the angular separation of q and the scattered projectile increases. E.g., the angular separation is 38° in panel (a) while it is 82° in panel (d). In all cases the binary maximum at small angle θ₂ is strongly scaled down such that the double-lobe pattern turns

Figure 3. Scattering (xz) plane triple-differential cross sections (TDCS) for ionization of the 1π_g, 1π_u, and 3σ_u orbitals of CO₂ as a function of the ejected electron emission angle θ₂ for scattering angles θ₁ = −5° ± 0.5°, −10° ± 1.5°, −15° ± 3° and −20° ± 4° as well as for ejected-electron energies E₂ = 5 eV ± 1.5 eV, 8 eV ± 2 eV and 15 eV ± 3 eV. Experimental data (solid circles with error bars) and theoretical results from MCDW-WM (thick magenta line) and MCDW (thin red line) are summed TDCS. Individual TDCS for 1π_g (green dashed line), 1π_u (blue dotted line), and 3σ_u (cyan dash dotted line) orbitals are obtained by the MCDW method. The vertical arrows indicate the momentum transfer direction +q and its opposite −q. The TDCS is given in atomic units (a.u.).
into a single lobe for $\theta_1 = -5^\circ$. At $\theta_1 = -10^\circ$ a residual shoulder shows up and only for $\theta_1 = -20^\circ$ there is a clear second lobe in the binary peak pattern.

Therefore, it can be concluded that the disappearance of the double-lobed binary peak pattern for decreasing scattering angles $\theta_1$ results from two reasons. Firstly, from increasing deviation from the above mentioned Bethe Ridge kinematics and, secondly, from stronger suppression of the peak at small angles due to PCI.

Comparing the experimental results to theoretical predictions from MCDW-WM in the scattering plane geometry, we see that the calculations generally show reasonable agreement with the experimental data concerning the shape of the cross section pattern. E.g. the binary peak is rather well reproduced concerning its angular position and its structure with a single peak for small scattering angles $\theta_1$ and a shoulder or a double peak for larger $\theta_1$. Concerning the recoil lobe there is disagreement in most cases concerning its angular position. Experimentally it is observed at larger angles than obtained by MCDW-WM theory (see, e.g. figures 3(b)–(d)). Here the recoil lobe position obtained by the MCDW calculation is in better agreement with experiment.

Finally, the magnitudes of the TDCSs in particular at larger scattering angles and higher ejected energies are overestimated by the MCDW-WM calculations, see e.g. figure 3(h) for $\theta_1 = -20^\circ$ and $E_2 = 8$ eV, figure 3(k) for $\theta_1 = -15^\circ$ and $E_2 = 15$ eV and figure 3(l) for $\theta_1 = -20^\circ$ and $E_2 = 15$ eV. Clearly inclusion of PCI is mandatory to reproduce the TDCS since the MCDW results in all cases

Figure 4. As figure 3 but for the perpendicular (yz) plane.
strongly overestimate the relative size of the binary peak in particular for small $\theta_1$ angle.

Figure 4 shows TDCS for the $yz$-plane (perpendicular plane), which is perpendicular to the scattering plane but contains the incoming projectile momentum $k_0$. For this plane, symmetry considerations require the cross sections to be symmetric about $\theta_2 = 180^\circ$ which can be seen in both theory and experiment. In cases where the polar angle of the momentum transfer is large (ideally $\theta_q = 90^\circ$) this plane probes the TDCS in the minimum in between the binary and the recoil peaks. Since these structures are due to a first order projectile target interaction the perpendicular plane regularly is studied in order to identify higher order contributions to the TDCS. Therefore, the TDCS in this plane can be a critical test of theory [50].

In the present case the perpendicular plane cuts through the binary peak in the forward direction for small angle $\theta_2 \approx 0^\circ/360^\circ$ and through the recoil peak for $\theta_2 \approx 180^\circ$. Therefore, in the MCDW calculation there is a strong maximum in the forward direction and a second weaker one in the backward direction. At $\theta_2 \approx 0^\circ/360^\circ$ PCI strongly scales down the binary peak such that the maximum turns into a minimum in the MCDW-WM result. While the experimental data do not cover small forward and backward angles two maxima are observed in the angular ranges $\theta_2 = 60^\circ$–$90^\circ$ and $\theta_2 = 270^\circ$–$300^\circ$, respectively. The MCDW-WM

Figure 5. As figure 3 but for the full perpendicular ($xy$) plane.
calculations show these maxima for higher ejected electron energy $E_2 = 15$ eV while for low energy $E_2 = 5$ eV the experimental maxima are not reproduced. Most striking is the discrepancy in the vicinity of the recoil peak close to $\theta_2 = 180^\circ$ where the theoretical results are too large, i.e. they show maxima while experiment shows minima except for $E_2 = 15$ eV.

A remark should be made concerning the maxima around $\theta_2 = 90^\circ$ and $\theta_2 = 270^\circ$ which have been observed regularly before for other targets like Ar, He, H$_2$ [51–53] and as mentioned above could be considered as resulting from higher order projectile-target interaction. MCDW is a first order model and as expected we see no indication of these maxima in the MCDW results. On the other hand maxima appear after multiplication with the WM factor. In the present case the maxima result from the steep rise of the MCDW TDCS for approaching the binary peak ($\theta_2 \rightarrow 0^\circ/360^\circ$) and the counteracting downscaling of the TDCS due to PCI around $\theta_2 \approx 0^\circ/360^\circ$. Since PCI can be considered as a higher order projectile-target interaction the previous interpretation in this sense is correct.

In the full perpendicular plane (xy plane), which is perpendicular to the incoming projectile direction, the ejected electron’s polar angle is fixed to $\theta_2 = 90^\circ$ and the azimuthal angle $\phi_2$ is varied from $0^\circ$ to $360^\circ$. In this plane experimentally the full $\phi_2$ angular range is accessible. In figures 5(a)–(l), experimental TDCS and theoretical results for the full perpendicular are compared. Again the cross sections are symmetric with respect to $180^\circ$. The binary and recoil peaks are observed in the vicinity of $\phi_2 = 0^\circ$ and $180^\circ$, respectively. The theoretical predictions of MCDW-WM and MCDW models in this plane are in reasonable agreement with the experimental data except for the strongly underestimated binary peak near $0^\circ$ and $360^\circ$ again for the kinematics of larger scattering angles and higher ejected electron energies. In figures 5(a)–(l), the shapes of the two theories are almost identical and only the magnitude differs from each other. This shows an interesting property of the perpendicular plane namely for small projectile scattering angles $\theta_1$ PCI is rather small and almost constant over the entire angular range $\phi_2$.

Finally, it is informative to compare the present results for the CO$_2$ molecule to those for Ne(2p) ionization. Ne(2p) was measured before by Pfüger et al under very similar kinematical conditions as in the present case [15]. The momentum profile of Ne(2p) has a single maximum at $k = 0.83$ a.u. [54] and, therefore is very similar to the spherically averaged momentum profiles of the 1$\pi_v$, 1$\pi_u$, and 3$\sigma_u$ orbitals with single maxima at $k = 0.8$ a.u. and 0.65 a.u., respectively. In the scattering plane the neon TDCS resembles the CO$_2$ TDCS in its general pattern but the TDCS variations of the binary peak are more pronounced, as, e.g., the central minimum is deeper and for Bethe Ridge conditions it goes almost down to zero. This shows that strong molecular effects are present for the CO$_2$ target. An example is scattering of the incoming and outgoing waves in the more complex multicenter potential which in the present MCDW model is described by a distorted wave. Moreover these distortion effects also depend on the particular properties of the ionized orbitals like their symmetries, such that the individual TDCS patterns are quite different from each other.

6. Conclusion

We presented a combined experimental and theoretical study of the electron-impact ionization of CO$_2$ for a projectile energy of $E_p = 100$ eV. The 3D momentum vectors of the final-state particles are determined using a reaction microscope. Experimentally, the summed TDCS for the ionization of 1$\pi_v$, 1$\pi_u$, and 3$\sigma_u$ orbitals leading to a stable CO$_2^+$ cation are presented in the coplanar, perpendicular and full perpendicular planes. The measured TDCS are inter-normalized across all scattering angles of $\theta_1$ from $-5^\circ$ to $-20^\circ$, and ejected-electron energies of $E_2$ from 5 to 15 eV.

The experimental TDCS were compared to predictions from a MCDW method. The relative cross section of this model which is established within the basis of the FBA with no inclusion of the PCI effects is significantly too high in the vicinity of the scattered projectile direction. The predictions from the MCDW-WM model, where PCI is accounted for via the WM approximation, clearly improve the results. Given the complexity of the target and the fairly low collision energy of 100 eV, the overall agreement of the MCDW-WM theory is reasonable. Most noticeable deviations are the angular positions of the recoil lobes. Furthermore, at higher scattering angles and ejected electron energies the MCDW-WM overestimates the overall cross section. In the perpendicular plane PCI could be identified to cause TDCS maxima outside the angular regions of the first order binary and recoil peaks.

The present study of electron impact ionization of a three-atomic molecule demonstrates that a plane wave first Born formalism can give reasonable results even at rather low projectile energy if a number of requirements are observed. Firstly, strongly asymmetric energy sharing is chosen and secondly, PCI between the continuum electrons is considered. Furthermore, accurate initial bound orbitals are employed and the interaction of the ejected electron with the multi-center ionic potential is accounted for.

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References

[1] Bartschat K and Kushner M J 2016 Proc. Natl Acad. Sci. USA 113 7026
[2] Alizadeh E, Orlando T M and Sanche L 2015 Annu. Rev. Phys. Chem. 66 379
[3] Ehrhardt H, Schulz M, Tekaat T and Willmann K 1969 Phys. Rev. Lett. 22 89
[4] Amaldi U, Egidi A, Marconero R and Pizzella G 1969 Rev. Sci. Instrum. 40 1001
[5] Ehrhardt H, Jung K, Knoth G and Schlemmer P 1986 Z. Phys. D 1 3
[6] Lahmam-Bennani A 1991 J. Phys. B: At. Mol. Opt. Phys. 24 2401
[7] Madison D H and Al-Hagan O 2010 J. At. Mol. Opt. Phys. 2010 367180
[8] Dürr M, Dimopoulou C, Dorn A, Najiari B, Bray I, Fursa D V, Chen Z, Madison D H, Bartschat K and Ulrich J 2006 J. Phys. B: At. Mol. Opt. Phys. 39 4097
[9] Ren X, Sentlieben A, Pfügler T, Dorn A, Bartschat K and Ulrich J 2010 J. Phys. B: At. Mol. Opt. Phys. 43 035202
[10] Rescigno T N, Baetertschi M, Isaacs W and McCurdy C 1999 Science 286 2474
[11] Bray I, Fursa D, Kadyrov A, Stelbovics A, Kheifets A and Mukamedzhanov A 2012 Phys. Rep. 520 135
[12] Zatsarinny O and Bartschat K 2011 Phys. Rev. Lett. 107 023203
[13] Ren X et al 2010 Phys. Rev. A 82 032712
[14] Ren X et al 2015 Phys. Rev. A 92 052707
[15] Pfügler T, Zatsarinny O, Bartschat K, Sentlieben A, Ren X, Ulrich J and Dorn A 2013 Phys. Rev. Lett. 110 153202
[16] Ren X, Amami S, Zatsarinny O, Pfügler T, Weyland M, Baek W Y, Rabus H, Bartschat K, Madison D and Dorn A 2015 Phys. Rev. A 91 032707
[17] Ren X, Amami S, Zatsarinny O, Pfügler T, Weyland M, Dorn A, Madison D and Bartschat K 2016 Phys. Rev. A 93 062704
[18] Al-Hagan O, Kaiser C, Murray A J and Madison D 2009 Nat. Phys. 5 59
[19] Ren X, Pfügler T, Xu S, Colgan J, Pindzola M S, Sentlieben A, Ulrich J and Dorn A 2012 Phys. Rev. Lett. 109 123202
[20] Colgan J, Pindzola M S, Robicheaux F, Kaiser C, Murray A J and Madison D H 2008 Phys. Rev. Lett. 101 233201
[21] Zammit M C, Savage J S, Fursa D V and Bray I 2016 Phys. Rev. Lett. 116 233201
[22] Li X, Ren X, Hossen K, Wang E, Chen X J and Dorn A 2018 Phys. Rev. A 97 022706
[23] Nixon K L, Murray A J, Chaluvadi H, Ning C, Colgan J and Madison D H 2013 J. Chem. Phys. 138 174304
[24] Buith-Williams J D et al 2013 J. Chem. Phys. 139 034306
[25] Ali E, Nixon K, Murray A, Ning C, Colgan J and Madison D 2015 Phys. Rev. A 92 042711
[26] Jones D B et al 2015 J. Chem. Phys. 143 184310
[27] Lahmam-Bennani A, Stiucu Casagrande E M and Naja A 2009 J. Phys. B: At. Mol. Opt. Phys. 42 235205
[28] Ozer Z N et al 2016 Phys. Rev. A 93 062707
[29] Alwan O, Chuluunbaatar O, Assfelf X, Naja A and Joulakian B B 2014 J. Phys. B: At. Mol. Opt. Phys. 47 225201
[30] Chuluunbaatar O and Joulakian B 2010 J. Phys. B: At. Mol. Opt. Phys. 43 155201
[31] Hussey M J and Murray A J 2005 J. Phys. B: At. Mol. Opt. Phys. 38 2965
[32] Chaluvadi H, Ning C G and Madison D 2014 Phys. Rev. A 89 062712
[33] Ren X, Amami S, Hossen K, Ali E, Ning C G, Colgan J, Madison D and Dorn A 2017 Phys. Rev. A 95 022701
[34] Li X, Gong M, Liu L, Wu Y, Wang J, Qu Y and Chen X 2017 Phys. Rev. A 95 012703
[35] Gong M, Li X, Zhang S B, Liu L, Wu Y, Wang J, Qu Y and Chen X 2017 Phys. Rev. A 96 042703
[36] Ward S J and Macek J H 1994 Phys. Rev. A 49 1049
[37] Ulrich J, Moshammer R, Dorn A, Dörner R, Schmidt L and Schmidt-Böcking H 2003 Rep. Prog. Phys. 66 1463
[38] Zhang S B, Li X Y, Wang J G, Qu Y Z and Chen X 2014 Phys. Rev. A 89 052711
[39] Sanna N and Gianturco F 2000 Comput. Phys. Commun. 128 139
[40] Sanna N and Morelli G 2004 Comput. Phys. Commun. 162 51
[41] Sanna N, Baccarelli I and Morelli G 2009 Comput. Phys. Commun. 180 2544
[42] Li X et al private communication
[43] Cook J P D and Brion C E 1982 Chem. Phys. 77 339
[44] Wang E, Shan X, Tian Q, Yang J, Gong M, Tang Y, Niu S and Chen X 2016 Sci. Rep. 6 39351
[45] Leung K T and Brion C E 1985 Chem. Phys. 93 319
[46] Frisch M J et al 2016 Gaussian16 Revision A.03 (Wallingford, CT: Gaussian)
[47] Becke A D 1993 J. Chem. Phys. 98 5648
[48] Lee C, Yang W and Parr R G 1988 Phys. Rev. B 37 785
[49] Dunning T H Jr 1989 J. Chem. Phys. 90 1007
[50] Schulz M et al 2003 Nature 422 48
[51] Ren X, Hossen K, Wang E, Pindzola M S, Dorn A and Colgan J 2017 J. Phys. B: At. Mol. Opt. Phys. 50 204002
[52] Dürr M, Dimopoulou C, Najiari B, Dorn A, Bartschat K, Bray I, Fursa D V, Zhangjin C, Madison D H and Ulrich J 2008 Phys. Rev. A 77 032717
[53] Ren X, Sentlieben A, Pfügler T, Dorn A, Bartschat K and Ulrich J 2011 Phys. Rev. A 83 052714
[54] Leung K T and Brion C E 1983 Chem. Phys. 82 87