

# Controlling ionisation and fragmentation processes in CO<sub>2</sub> via inelastic electron recollisions

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**Abstract.** The angular dependence of nonsequential double ionisation and dissociation induced by laser driven inelastic electron rescattering was investigated experimentally in aligned CO<sub>2</sub>. A clear dependence on the recollision angle was found demonstrating quantum control of ionisation and dissociation processes in the strong field regime.

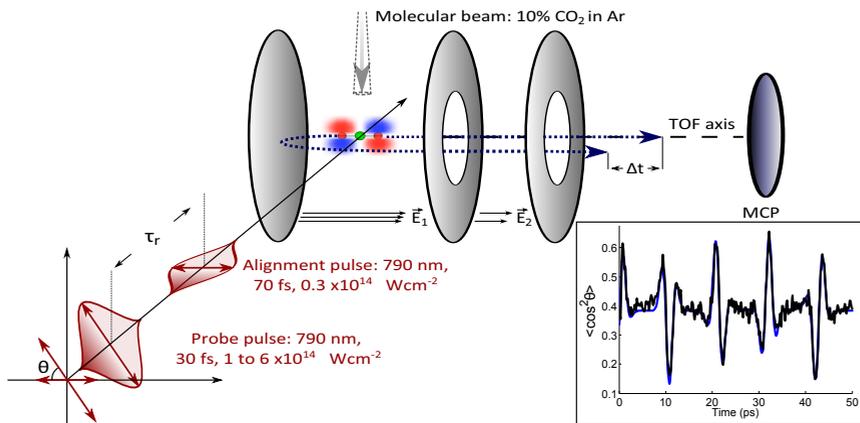
## 1 Introduction

Being able to control physical processes down to the molecular level is an ongoing challenge in modern day science and requires high resolution structural and dynamic information in this regime. Over the past decade laser driven electron recollision has established itself as a versatile tool to probe ultrafast molecular dynamics with techniques combining sub-ångstrom spatial with sub-femtosecond time resolution [1]. Laser driven electron recollision describes a set of effects, where a strong laser field tunnel-ionises an atom or molecule and drives the freed electron into the continuum. Due to its oscillatory motion the electron is eventually accelerated back to the parent ion. Upon recollision the electron may recombine to its original ground state, leading to the widely studied phenomenon high harmonic generation (HHG) [2]. Yet only during an inelastic recollision does the free electron itself induce molecular processes, hence offering not only a tool to probe but also to control the related dynamics. It is against this backdrop of research that we present the angular dependence of recollision induced ionisation (nonsequential double ionisation, NSDI) and dissociation channels in CO<sub>2</sub> with respect to its molecular axis. NSDI has been studied in several molecules and has previously been observed in CO<sub>2</sub> below intensities of  $2 \times 10^{14} \text{ Wcm}^{-2}$  at 800 nm [3]. So far the full angular distribution of this process has not been measured in molecules. It is further known that NSDI can proceed either via direct electron knockout or excitation of the parent ion with subsequent field ionisation. The latter is favoured at low intensities in the multiphoton regime. This transition has only been observed in N<sub>2</sub> and O<sub>2</sub> via cold target ion recoil momentum spectroscopy (COLTRIMS) [4,5]. A study by McKenna [6] has identified dissociative excitation as a major contribution to the predissociation channels  $\text{CO}_2^{+*} \rightarrow \text{CO}^+(^2\Sigma^+) + \text{O}(^3P)$  and  $\text{CO}_2^{+*} \rightarrow \text{O}^+(^2D) + \text{CO}(^1\Sigma^+)$  over an intensity range of about 1 to  $8 \times 10^{14} \text{ Wcm}^{-2}$ . It is known from several studies that these channels result in fragments with zero kinetic energy release (KER) [7], which ensures their full collection in the present setup. We will refer to the corresponding fragment ions as  $\text{CO}_{(1,0)}^+$  and  $\text{O}_{(1,0)}^+$ , indicating the distribution of the available charge in these channels.

## 2 Experiment

The experimental scheme is shown in figure 1 and consists of a pump-probe setup employing impulsive molecular alignment and a time-of-flight mass spectrometer (TOFMS) for identifying the resulting ion

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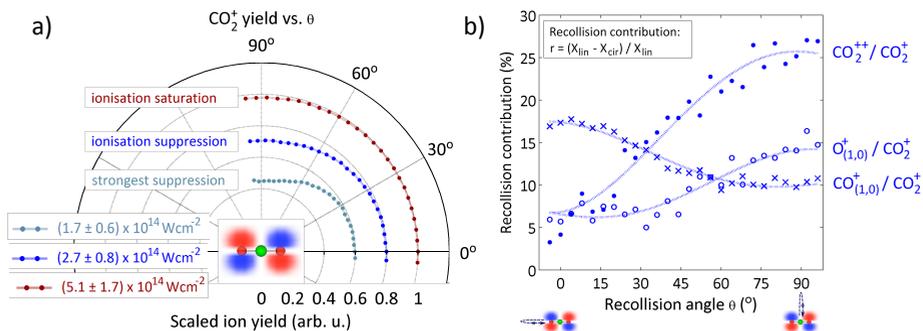


**Fig. 1.** Illustration of the employed experimental scheme (see text for details) and a characteristic alignment revival obtained as described in [9] (in black) together with the simulated expectation value  $\langle \cos^2 \theta \rangle$  (in blue).

species and their respective channels. The TOF mass spectrometer is operated under Wiley-McLaren space focusing conditions [8]. Here, the electric acceleration field between the electrodes ensures that the flight time of each ion created in the interaction region is proportional to its mass to charge ratio  $\sqrt{m/q}$ . As indicated in fig.1, for molecules aligned along the TOF axis, the kinetic energy release (KER) of their fragment ions separates them in time, as the fragment ejected away from the detector needs additional time to turn around. This effect separates the dissociation channels with higher KER from the zero KER channels  $\text{CO}_{(1,0)}^+$  and  $\text{O}_{(1,0)}^+$ . Seeding small molecules in Ar leads to a significant improvement of rotational cooling when undergoing a supersonic expansion, which can be attributed to the increased number of collisions between the molecules and the atoms. For this, a significant enhancement of alignment quality is achieved when seeding 10%  $\text{CO}_2$  in Ar [9], improving the contrast of the measured angular dependences. A typical revival scan is shown in the inset of fig.1 (details can be found in [9]) and gives a maximum alignment of 0.64 at a delay of 31.4 ps. In order to disentangle the recollision from the ionisation step, the angular dependence of the single ionisation yield of  $\text{CO}_2$  is determined at the same time. This angular dependence is taken into account in the analysis of the angular distribution of the obtained ion yields. In order to identify the recollision process, the ion yields from a circularly polarized probe pulse are recorded, as recollision is switched off in this case. For a meaningful comparison, one has to ensure that the single ionisation rates in the linearly and circularly polarized fields are the same. This is achieved using the atomic argon already present in the gas mix. The yield of a given ion at a given KER is obtained by numerically integrating the corresponding peak in the TOF spectrum. The difference in the ion yields of species  $X$  between linear and circular polarisation identifies the recollision contribution and is defined by  $r = \left[ (X/\text{CO}_2^+)_{(lin)} - (X/\text{CO}_2^+)_{(circ)} \right] / (X/\text{CO}_2^+)_{(lin)}$ .

### 3 Results and discussion

Figure 2a shows the angularly resolved single ionisation rate of  $\text{CO}_2$  for three intensities. We measured a clear angular dependence partially reflecting the highest occupied molecular orbital (HOMO) of  $\text{CO}_2$  with a nodal plane at 90 degrees. The other nodal plane, expected at 0 degree, is not visible in this data. This is most likely due to ionisation from lower lying orbitals HOMO-2 or HOMO-3 having a  $\sigma$  geometry and from the convolution of the signal with the angular distribution width of the molecules. By reducing the intensity, one can clearly see the transition from an ionisation saturation regime with an almost isotropic ionisation rate to an angular modulation of the single ionisation yield. Fig.2b shows the angular dependence of NSDI and fragmentation for an intensity of  $(2.7 \pm 0.8) \times 10^{14} \text{ Wcm}^{-2}$ , which corresponds to a maximum recollision energy of  $50 \pm 15 \text{ eV}$  and a Keldysh parameter of  $\gamma =$



**Fig. 2.** Experimental results at a pump-probe delay corresponding to a maximum alignment at about 31.4 ps pump-probe delay. a) relative ionisation yield of  $\text{CO}_2^+$  ions as a function of recollision angle for three different intensities. b)  $\text{CO}_2^{2+}$  NSDI,  $\text{CO}_{(1,0)}^+$  and  $\text{O}_{(1,0)}^+$  ion yields due to recollision at the medium probe intensity of  $2.7 \pm 0.8 \times 10^{14} \text{Wcm}^{-2}$  and corrected with respect to the single ionisation step.

$0.7 \pm 0.2$ . For  $\text{CO}_2^{2+}$  NSDI, a clear angular signature is observed with a strong suppression for electron recollision along the molecular axis. It was found that at intensities below  $2 \times 10^{14} \text{Wcm}^{-2}$  this angular dependence becomes almost isotropic at a recollision contribution of about 50 %. This is interpreted as a transition to the multiphoton regime with the direct electron impact scenario becoming invalid. A Keldysh parameter of  $\gamma \approx 1$  and a recollision energy close to the second ionisation potential  $I_p^+ = 22.4 \text{ eV}$  support this view. As for  $\text{CO}_2^{2+}$  NSDI, a clear angular signature can be observed in the  $\text{CO}_{(1,0)}^+$  and  $\text{O}_{(1,0)}^+$  channels. Surprisingly, the two channels show a nearly opposite behaviour. While it is known that they compete at excitation energies below 19.6 eV [7], it is likely that distinct angular electron impact cross-sections are revealed in this measurement. However, it is not clear at this point that recollision is the sole cause for the observed angular dependence. Varying the probe laser ellipticity will answer this question unambiguously [10].

## 4 Conclusion

For the first time, the angular dependence of double ionisation and dissociation induced by laser driven inelastic electron rescattering has been investigated experimentally in aligned  $\text{CO}_2$ . A strong dependence on the recollision angle in NSDI and dissociative excitation was shown in the tunneling regime. Here, the opposite behaviour of  $\text{CO}_{(1,0)}^+$  and  $\text{O}_{(1,0)}^+$  channels is a novel result. Moreover, the transition to the multiphoton regime for NSDI in  $\text{CO}_2$  is observed for the first time. These results demonstrate the potential of inelastic electron recollisions for probing and controlling electron dynamics in molecules, as NSDI could be switched on or off and the dominating fragmentation channel chosen via the electron recollision angle.

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