STUDYING THE DISSOCIATION DYNAMICS OF CARBON DIOXIDE

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If I were not a physicist, I would probably be a musician. I often think in music. I live my daydreams in music. I see my life in terms of music. Albert Einstein

ABSTRACT

Small molecules, and their fragmentation to smaller constituents upon excitation, are often used to understand how the bonds in a molecule are formed and how they break. One of such widely studied model molecule is CO_2 .

This study aims at extending the knowledge of dissociation of carbon dioxide by measuring also the negatively charged fragments. In addition, these anions are linked to positive ions (cations) which are more abundant, and their production pathways are widely studied. The measurements were carried at *Elettra* Synchrotron Radiation Laboratory in Trieste, Italy. Provided that anion production at corelevel excitation is far less abundant than that of electrons and cations, a new spectrometer was developed precisely for the purpose of detecting the negative ions. It works in tandem with a positive ion spectrometer, mounted together for coincidence measurements. The properties and advantages of the present instrument, such as high acceptance angle and magnetic deflection of unwanted electrons are described.

 $\rm CO_2$ molecule is excited by photons which are energetic enough to promote core electrons of the oxygen atom to unoccupied molecular orbitals in $\rm CO_2$ - the following dissociation pathways are then studied by time-of-flight based mass spectroscopy. Both singlycharged and doubly-charged cations are found, in varying proportions, at different photon energies. Also, negative ions are seen, with $\rm C^-$ being present only at the O1s edge but not at lower excitation energies. Furthermore, metastable states and triply-charged cations are a possibility, however, their complete analysis requires more attention. They are nonetheless discussed and analyzed to some extent.

POPULAR SCIENCE WRITING (IN ROMANIAN)

Dioxidul de carbon este unul dintre cei mai importanți compuși chimici pentru susținerea vieții pe Terra. Acesta joacă un rol crucial în procesul de fotosinteză prin care plantele reglează natural cantitatea necesară de oxigen din atmosferă pentru ființele aerobe, inclusiv oamenii.

Acesta a fost descoperit in anul 1640 de către Jan Baptist van Helmont care a observat că în urma procesului de ardere al cărbunelui, este o diferență substanțială de masă între produsul initial (cărbunele) și rămășițele rezultate (cenușa). Fizicianul antemenționat a atribuit apariția decalajului unei substanțe invizibile pe care a numit-o gaz sau "spiritus silvestre" (spirit sălbatic), CO_2 devenind astfel primul gaz considerat compus chimic de sine stătător. Odată cu dezvoltarea științelor naturii (fizică, chimie) s-a ajuns la concluzia că este format din micro-particule numite molecule care, la randul lor sunt formate din așa numiții atomi, cei din urmă formând legături pentru a constitui moleculele. Aceste legături au putut fi explicate mai târziu (secolul XX) cu ajutorul mecanicii cuantice.

Dioxidul de carbon este un gas incolor, inodor în concentrații scăzute, prezentând un miros înțepător la concentrații ridicate. Este de aproximativ 1.6 ori mai dens decât aerul și nu poate fi lichefiat în condiții normale de presiune (doar la presiuni înalte). Racit la temperaturi sub -78.5⁰C acesta devine solid, formând astfel gheața carbonică sau gheața "uscată", întâlnită deseori în industrie.

O posibilitate de a studia molecula de CO₂ este prin iradiere cu raze X. Razele X sunt lumină de energie mai înaltă comparativ cu lumina vizibilă percepută de ochiul uman, iar energia este purtată de așa numiții fotoni. Atomii de oxigen și carbon ce constituie molecula sunt formați din protoni, neutroni și electroni. Protonii și neutronii formează nucleele atomice iar electronii "orbitează" în jurul acestora pe orbitali electronici. În interacțiunea lor cu radiația, electronii pot "sări" pe un orbital superior sau pot părăsi molecula, promovând astfel sistemul într-o stare energetică superioară sau într-o stare de ionizare. Mecanica cuantică spune că energia luminii incidente trebuie să fie precis potrivită cu diferențele valorilor energetice aferente orbitalilor în discuție, energii de obicei în domeniul razelor X.

Datorită nevoilor ridicate de precizie a energiei radiatiei, precum si intensitătii luminoase, sursele conventionale de raze X nu sunt întotdeauna cele mai bune alegeri în astfel de experimente. Se poate apela însă la radiatia sincrotronului, un accelerator de particule circular care creste energia electronilor la valori înalte (la viteze apropiate de viteza luminii). Pentru a avea o idee de vitezele implicate, luăm un calcul simplu pentru actualul sincrotron de la MAX IV din Lund. Având în vedere că acesta are 532 m în circumferintă si electronii se deplasează cu 99.99 % din viteza luminii (300.000 km/s), vor parcurge acceleratorul de peste 500.000 de ori pe secundă. Electronii sunt trimisi în elemente magnetice construite pentru a imprima oscilatii traiectoriei lor, fiecare electron producând astfel un foton la fiecare "curbă" pe care o face. Energia radiatiei produse depinde de energia electronilor si de intensitatea câmpului magnetic la care sunt supusi, facând astfel posibilă reglarea ei cu mare acuratete. În plus, numărul fotonilor produsi este ridicat, asigurând astfel un flux cu câteva ordine de mărime mai consistent decât în cazul surselor obisnuite (i.e. intensitate luminoasă ridicată).

Asadar, avem calea de a aduce molecula într-o stare energetică excitată sau ionizată. În cazul ionizării, molecula nou formată (cu un electron lipsă) devine instabilă și, ca toate entitătile din natură, tinde la echilibru. Una dintre metodele de dezexcitare este ruperea în fragmente ionice moleculare formate din atomii constituenți. Având în vedere că fragmentele nu sunt neutre d.p.d.v. electric (de aceea numite ionice), în prezența unui câmp electric exterior vor putea fi accelerate in directii diferite (diferenta venind în urma semnului sarcinii + sau -). Spectroscopia bazată pe "timpul de zbor" măsoară timpul pe care aceste fragmente îl fac de la producere până la detectarea lor. Astfel, se pot identifica fragmentele respective, informații utile pentru determinarea modelului după care moleculele disociază, obtinând astfel informatii esentiale despre structura moleculară. Această lucrare descrie în detaliu metodele folosite la investigarea proprietătilor mentionate mai sus precum si rezultatele experimentale despre disocierea moleculei de dioxid de carbon.

POPULAR SCIENTIFIC INTRODUCTION

Carbon dioxide is one of the most important chemical compounds to support life on Earth. It plays a crucial role in the process of photosynthesis through which plants naturally regulate the oxygen quantity from the atmosphere for aerobic beings, including humans.

CO₂ was discovered in 1640 by Jan Baptist van Helmont who observed that after burning coal, there is a noticeable difference in mass between the initial product (coal) and the remains (ash). He then suggested the occurrence of an invisible substance he later named gas or "spiritus silvestre" (wild spirit), making carbon dioxide the first gas to be considered as an isolated chemical compound. With the development of natural sciences, especially physics and chemistry, it was concluded that there are micro-particles that form the gas, called molecules, which have atoms as constituent parts, held together by molecular bonds. This could only be explained later on, with the development of quantum mechanics.

Carbon dioxide is a transparent gas, odorless in low concentrations, presenting a sharp odor in high concentrations. It has a density roughly 1.6 times higher than air and cannot be liquefied in normal pressure conditions (only at high pressures). When cooled under a temperature of -78.5°C it becomes solid, thus forming carbonic ice, also known to industry as "dry ice".

One way of studying the CO_2 molecule is by the means of X-ray irradiation, thus allowing for processes such as photoabsorption (absorption of light), photoionization (ejecting electrons by photoabsorption) and photodissociation ("breaking" the molecule after photoabsorption and ionization). X-ray light is outside the human visible spectrum, it has higher energy (shorter wavelengths) and has the capacity to penetrate matter.

The oxygen and carbon atoms which make the molecule are formed by electrons, protons and neutrons. The latter two form the atomic nuclei, having electrons "orbit" around them on circular-like paths called orbitals (this is not exactly true, but it is accurate enough for present explanations). When interacting with X-rays, electrons can "jump" on an energetically higher orbital or can even be completely ejected from the system, thus promoting the atom/molecule in an excited or ionized state. Quantum mechanics states that the energy of the light must be precisely matched with the transition energy and for inner shell electrons these energies fall in the X-ray regime.

Due to the high precision demands in tuning the light, conventional X-ray sources are not the desired choices for such experiments. One way of satisfying the strict requirements is by using light emitted by a synchrotron, a circular accelerator which increases the energy of electrons to very high values (attaining velocities close to the speed of light). In order to form an idea about the magnitudes involved. we consider a simple situation at the new MAX IV synchrotron in Lund. We know it had a circumference of 532 m and that electrons moving at roughly 99.99% of the speed of light (approx. 300.000.000 m/s) will do more than 500.000 turns in the accelerator every second. Energetic electrons are passing magnetic arrays, called undulators that will force a curved trajectory on the beam. With every such oscillation, each electron will emit photons in the plane of oscillation with energy defined by the energy of the electrons and the magnetic field strength. The latter is adjustable, thus assuring a wide range of energies for the produced light. Furthermore, the photon flux is considerably higher than at any conventional sources, so synchrotrons provide high intensity X-rays, should they be required.

So far, we have seen the ways of promoting the molecule into energetically higher states. If ionization is considered, the newly formed positively charged ion (with at least one electron missing) is unstable and, like all entities from nature, it tends to reach a state of equilibrium. One of the decay mechanisms is breaking into smaller fragments formed by its constituent atoms. Considering the fragments are not electrically neutral (this being the reason they are called ionic), in the presence of an electric field they will be accelerated in different directions (the difference arising from the sign of the charge + or -). Time of flight mass spectroscopy measures the time these fragments take from creation to detection, thus identifying them by coincidence measurements. This information is then used to determine the dissociation pathways of the studied molecule. This work describes the methods used in investigating the aforementioned properties, followed by conclusions and discussion regarding the interpretation of data.

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ABBREVIATIONS

TOF	Time of flight
PEPICO	Photo-electron positive ion coincidence
NIPICO	Negative ion positive ion coincidence
PIPICO	Positive ion positive ion coincidence
NIPIPICO	Negative ion positive ion positive ion coincidence
PEPIPICO	Photo-electron positive ion positive ion coincidence
LCAO	Linear combinations of atomic orbitals
SALC	Symmetry adapted linear combinations
MO	Molecular orbital
TDC	Time to digital converter
PIY	Positive ion yield
NIY	Negative ion yield
IP	Ionization Potential

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CHAPTER 1

INTRODUCTION

Carbon dioxide is one of the most important compounds to sustain life on Earth. It is a crucial gas in the process of photosynthesis, by which plants naturally regulate the oxygen balance required by aerobic beings.

In 1640 [3] Jan Baptist van Helmont noticed that from the process of burning charcoal, the mass of the remains was significantly lower than the mass of the initial charcoal. He deduced that the difference rose due to an invisible substance which he called "gas" or "spiritus silvestre" (wild spirit [4]), making CO_2 the first gas considered as a discrete chemical compound. Scientific advances in the fields of physics and chemistry made it clear that carbon dioxide gas is made up of small constituents called molecules which, in turn, are formed by even smaller parts called atoms that bond together to form molecules. Later, by the development of quantum mechanics, the bonding mechanism could be explained.

Carbon dioxide is a colorless, odorless (at lower concentrations) gas, having a standard conditions density of 1.98 kg/m^3 [4]. Below pressures of 5.1 atm, CO₂ has no liquid state at low temperatures, it becomes solid at roughly 194 K (~ -80°C), state commonly known as dry ice.

A suitable way of studying and analyzing the CO_2 molecule is by investigating its interaction with light. In order to successfully do so, one needs to carefully tune the wavelength of the light so as to match the discrete energy levels of the molecule. This can be achieved at a synchrotron light facility, where energy adjustment is solved by the use of tunable undulator light sources. With photo-absorption experiments, the molecule can be excited to higher energy states or ionized. More energetic radiation induces the creation of a so called core-hole state, where an electron from the core of the atom (inner shells) is promoted to a higher energy or continuum state, calling it core-electron excitation or ionization. From these states, often via some intermediary states, the molecule will rupture into smaller fragments via dissociation.

When dissociation leads to ionic fragments, time of light (TOF) based mass spectroscopy can be used to analyze them. Charged particles with different masses are discerned by distinct flight times reflecting different mass-to-charge ratios (M/q). In order to study dissociation dynamics, one makes use of coincidence measurements with TOF spectroscopy, where charged particles are detected in coincidence with each other so as to ascertain which originated from a certain event, thus receiving more information from the ionization after interaction with light to the constituent fragments and, allowing for the construction of the dissociation pathways more reliably.

This work aims to describe fragmentation and dissociation of carbon dioxide molecule at core-level energies (O1s) by means of time of flight mass spectroscopy.

CHAPTER 2

MOLECULAR THEORY

A system consisting of bound electrons and two or more atomic nuclei is called a molecule. They are held together by chemical bonds, such as covalent bonds and ionic bonds. In order to describe molecules theoretically, one needs to adopt a quantum mechanical approach. This chapter aims at briefly describing the molecule, molecular symmetry and orbitals as theoretical grounds to the level required to follow the motivation for the experiments presented in this work.

2.1 Quantum approach

In quantum mechanics, any system can be described by the timeindependent Schrödinger equation:

$$H\Psi(r) = E\Psi(r) \tag{2.1}$$

with Ψ the wave function, E the system energy and H the Hamiltonian. For molecules, the Hamiltonian can be written as [5]:

$$H = -\frac{\hbar^2}{2m} \sum_{i} \nabla_i^2 - \sum_{N} \frac{\hbar^2}{2M_N} \nabla_N^2 + V(\vec{R}, \vec{r})$$
(2.2)

which takes into account *i* electrons, *N* nuclei, each with mass M_N and the interactions between them. The summation over *i* represents the electronic kinetic energies and *V* the Coulomb potential due to electrostatic attraction and repulsion forces. In other words, it describes the position and motion of electrons as they are attracted towards nuclei and repelled by other surrounding electrons. This being said, with increasing number of particles, solving the Schrödinger equation analytically proves to be very tedious work and is furthermore impossible for more complex systems, such as polyatomic molecules, therefore approximations are required for simplification.

A first assumption to be made is that the wave functions of electrons and nuclei are separable and can be written as:

$$\Psi_{mol}(\vec{r}_i, \vec{R}_N) = \psi_{el}(\vec{r}_i, \vec{R}) \chi_{nuc}(\vec{R})$$
(2.3)

where Ψ_{mol} denotes the molecular wave function, ψ_{el} the electronic wave function and χ_{nuc} the nuclear wave function. With this in mind, the following approximation states that $\nabla_N \psi_{el}$ (the derivative of the electronic wave function with respect to nuclear coordinates) is negligible or, in other words, due to the fact that nuclei are considerably heavier than electrons (at least by a factor of a thousand - the nucleus of the hydrogen atom, i.e. a proton, is 1836 times heavier than an electron) they can be thought of as stationary. Furthermore, electrons are expected to relocate according to the potentials created by the nuclei instantaneously. This is called the Born-Oppenheimer approximation, named after physicists Max Born and R. J. Oppenheimer in 1926 [6].

Now, if we rewrite the Schrödinger equation with the separable wave functions, it yields a new set of wave functions which in turn correspond to a set of discrete energy levels. This tool made it easier to perform calculations of wave functions and energies for more complex molecular systems. Should one plot the aforementioned energy values as a function of internuclear distance R, the potential energy curves are revealed, as illustrated in Fig. 2.1.

One immediate observation states that, if $R \to 0$ then $E \to \infty$ or the repulsion between the nuclei grows with decreasing internuclear distance (of course, due to electrostatic repulsion). In Fig. 2.1 one notices minima in the neutral and excited state curves. This is a state where the molecule reaches an energetically stable geometry, therefore it is referred to as bonding. The other curve (with no minimum) can be anti-bonding or non-bonding, states which do not allow for an energetically stable configuration.

2.2 Light-matter interaction

The main tool in studying molecules and their dynamics is by their interaction with light. An atom or a molecule that sees incident light may absorb one or several photons, should they be of appropriate energy. This section aims at briefly explaining the interaction of electromagnetic radiation with matter.

By absorption of a photon, the initial molecular energy state E_i is altered to a different state (or value) E_f by the following condition:

$$E_f - E_i = h \, \nu \tag{2.4}$$

where hv is the photon energy. One can also consider an ionized state as a final state, then consisting of a nucleus, bound and emitted electrons, as illustrated in Fig. 2.2.



Figure 2.1: Potential curves in the neutral and excited states of a system with the vibrational wave functions and a probable transition, showing the dependence of energy (E) as a function of internuclear distance R.

Other excitation mechanisms can be by particle collisions (e.g. electrons, protons, ions) but describing them is beyond the purpose of this work, thus I shall restrain to photons. By studying the aforementioned process and the absorption spectrum, it allows to construct the related energy levels of the molecule. An example of CO_2 absorption at oxygen core-level energies is depicted in Fig. 2.3. The spectrum shows structures corresponding to exciting the coreelectrons to unoccupied molecular orbital (π^*) and excitations to more atomic-like orbitals (3s, 4s and 4p, for example).

During absorption, an electron is removed from a filled molecular orbital and relocated to a different unoccupied orbital corresponding to a higher energy. If the bound electron is promoted to an empty bound orbital, this will take the molecule into a neutrally excited state and the process will be referred to as resonant photoabsorption.

If the incident radiation is energetic enough, an electron from the outer shells will be completely expelled from the atomic/molecular orbital and this process is known as ionization. Should the energy increase even further (several hundred eV) a core-electron can be



Figure 2.2: Light-matter interaction. Case a), the incident photon is absorbed and an electron is promoted to a higher energy state; b) shows the process of ionization when, after absorption, the electron is completely relocated outside the atomic or molecular system.

ejected, i.e. core-level ionization can occur. The energy of the incoming X-ray photon must be tuned to the ionization energy of the said core-electron and this tunability is attainable at a synchrotron radiation facility (as described later in Ch. 3.1).

Another matter to consider when it comes to photo-absorption is the cross-section, the probability a photon has to be absorbed by the studied compound. For the C1s and O1s core excitations of CO_2 , X-ray absorption cross-section measurements were performed by Truesdale *et al* and the results reveal a quick drop after resonance energies i.e. ionization cross section is at maximum at the ionization threshold of each orbital and it drops monotonically towards higher photon energies. Therefore, valence ionization cross-section show very low values at these energies and thus, only core-electron excitations are generally expected to be dominant in these cases.

2.3 Franck-Condon approximation

Similar to the Born-Oppenheimer approximation, electrons being over a thousand times lighter than nuclei, electronic transitions can occur faster than nuclei have time to adjust (or relocate accordingly). This is called the Franck-Condon approximation, and it assumes a stationary nucleus during electronic transitions on different energy levels. In actuality, the nucleus vibrates, however, due to the enormous weight difference and short electronic transition times (can be thought of as almost instantaneous) one can assume a nucleus as "fixed" during this process. Another implication is that in the



Figure 2.3: Carbon dioxide absorption spectrum at core-level energies, with the resonance at 535.4 eV[1] and other possible transitions, including the Ionization Potential (IP) of 541.2 eV[2]. Data recorded at *Elettra, Gas Phase beamline,* in Trieste, Italy.

frame of potential curves, electronic transitions can be considered as "jumps" in the vertical direction, as illustrated in Fig. 2.1.

Fig. 2.1 also shows the so-called Franck-Condon region (delimited by the two most probable transitions) a zone where transitions are more likely to occur. If one takes into account the wave functions of the initial and final states, one notices a vibrational part $|v_i\rangle$ and $|v_f\rangle$. The maximum likelihood of an electronic transition to take place is where the vibrational wave functions have the most overlap or, $|\langle v_i|v_f\rangle|^2$ is largest. The latter is called a Franck-Condon Factor (or FCF) and can be calculated numerically or deduced experimentally.

2.4 Molecular Symmetry

When evaluating molecular orbitals (MOs), symmetry plays an important role due to the fact that it simplifies calculations by a great amount, as shall be seen in the following. A symmetry property states that when a certain symmetry operation is applied to an object, it will leave said object unchanged. One can distinguish five types of symmetry operations:

- E - the identity operation

- C_n - n-fold rotation around an axis at angles $2\pi/n$

- σ - reflection through a mirror plane: vertical (σ_v), horizontal (σ_h), diedral plane (vertical plane that bisects the angle between two C_2 axes, σ_d) [7]

- i - inversion through a center of inversion

- S_n - n-fold improper rotation - rotation of the molecule by $2\pi/n$ and reflection on the perpendicular plane of the rotation axis

 C_n , the n-fold rotation with respect to an axis of symmetry consists of a rotation through angles $2\pi/n$ and it is of particular interest for the carbon dioxide molecule. Provided that CO_2 has a linear structure, as depicted in Fig. 2.4, it exhibits C_{∞} due to the fact that any rotation about its symmetry axis will leave it unchanged. Furthermore, it also has mirror plane reflection σ , in the center of inversion i (the carbon atom), perpendicular to its principal axis (horizontal), therefore denoted σ_h .

Molecules can be classified based on their symmetry properties into groups such as C_s (DNA molecule), C_2 (H₂O₂), $C_{2\nu}$ (H₂O) [8]. Given that carbon dioxide molecule has C_{∞} infinite fold rotation axis, infinite other C_2 two-fold axes perpendicular to C_{∞} and a horizontal mirror plane σ_h , it belongs to $D_{\infty h}$ symmetry group. The molecule along with the aforementioned symmetries is illustrated in Fig. 2.4.





Molecular orbitals, like atomic orbitals, are defined by the electronic wave functions. However, deducing molecular orbitals from performing calculations in the molecular Hamiltonian can become very complicated, even in the previously discussed Bohr-Oppenheimer approximation. What one does is rather construct them by using linear combinations of the constituent atomic orbitals (or LCAO) [9]:

$$\Psi = \sum_{r} c_r \Phi_r \tag{2.5}$$

where Ψ is the molecular orbital (also denoted MO), Φ_r atomic orbitals and c_r numerical factors. Even in this situation, one can end

up with plenty possible combinations of atomic orbitals. The likelihood of certain MOs to form is further determined by symmetry conditions, reducing the complexity in defining the MOs.

If a molecule holds particular symmetry properties (other than identity), group theory can state which atomic orbitals make contributions in forming the molecular orbitals due to net overlapping (having non-zero overlap integrals S, S \neq 0). Orthogonal atomic orbitals cannot combine, as they will have zero overlap, S=0. Furthermore, even with fulfilling the symmetry conditions, there are several other aspects one needs to consider when constructing the MOs. It is natural to think that the overlap will be small for atomic orbitals of very different energies thus, the atomic orbitals of the same energy dominate the bonding. Also, if one orbital is very compact (strongly localized inner-shell orbital), and the other is a diffuse valence orbital, their overlap contribution will not be sufficient.

2.5 Molecular orbitals of CO₂

I shall further summarize an approach to constructing the CO_2 molecular orbitals by considering the overlap between oxygen orbitals with the orbitals of the central carbon atom. As a simplification, it is convenient to reduce the $D_{\infty h}$ to D_{2h} , so as not to perform calculations using infinite-fold axes. Also, assigning coordinates to the atoms in the molecule makes the procedure more convenient.



Figure 2.5: Coordinate axes as chosen for carbon dioxide molecule.

The combinations of the two oxygen orbitals chosen that respect the symmetry conditions are based on 2*s* and 2*p* $(2p_z, 2p_y, 2p_x)$ [10], as seen in Fig. 2.7.

Now considering symmetry properties, one finds that these representations are reducible and can be matched to the orbitals of the central atom, in this case carbon, illustrated in Fig. 2.6.

Combining all reduced representations of the group orbitals corresponding to the oxygen atoms and the carbon atom orbitals, one



Figure 2.6: A sketch of carbon atom orbitals with their symmetry labels corresponding to the D_{2h} group - to be matched to orbitals from the oxygen atoms.



Figure 2.7: Schematic presentation of orbitals of the oxygen atoms.

ends up with molecular orbitals for the carbon dioxide molecule, as seen in Fig. 2.8.

2.6 Decay of excited states

The previously described excitations can occur both with electrons from the outer valence shells or inner shells, depending on the incoming radiation or energy of the incident particles. The electrons from the inner orbitals are called core-electrons and they are of interest in the field of photo-absorption spectroscopy, as such an excitation will form a core-hole, bringing the system in a very unstable, high energy state, from which it will decay rather quickly (a few femtoseconds for CO_2 molecule [11]) via radiative or non-radiative processes.



Figure 2.8: Carbon dioxide molecular orbitals with specifications of bonding, non-bonding and anti-bonding orbitals.

2.6.1 Fluorescence

A radiative decay process is called fluorescence. It consists of exciting a core-electron above the ionization threshold, thus ejecting it, leaving the ionic fragment in an unstable energy state. The created corehole will be filled by an outer shell electron and the excess energy will be released as a photon (typically in the X-ray regime). Fluorescence process is illustrated in Fig. 2.9. This decay can also occur via excitation onto a bound orbital (non-ionization), when the electron decays to a lower energy orbital, process known as resonant inelastic X-ray scattering.





2.6.2 Auger decay

In the field of electron/ion spectroscopy the non-radiative decay mechanism is of particular importance. This presumes the core-hole to be filled by an outer-shell electron, creating enough excess energy (from the relaxation) to completely eject another electron from the atomic or molecular system. This process is called Auger decay, named after physicist Pierre Auger who firstly explained it in 1923 [12] (having been observed and published by the Austrian-Swedish physicist Lise Meitner in 1922 [13]), shown in Fig. 2.10. There is also the possibility of exciting a core-electron to a bound, empty orbital and the decay process from such a state shall be referred to as resonant Auger decay.



Figure 2.10: Illustration of Auger decay mechanism, from absorption of an X-ray photon. The core-electron is removed and the core-hole is refilled by a relaxation process from another shell. The excess energy is released via an ejected Auger electron.

However, emission of a photon might also arise in this situation

due to the so called radiative Auger decay [14]. This presumes the relaxation to happen through emission of an X-ray photon along with promoting an electron either to a bound or continuum state. However, the probability of occurrence for such an event is considerably lower than for fluorescence, as the relaxation takes place via dipole-allowed transitions [15].

2.6.3 Fragmentation of CO₂

Molecular dissociation is a process in which molecules break into their constituents (smaller molecules, atoms, ions) by different means of external excitation. Fragmentation is a particular type of molecular relaxation and it implies the dissociation of unstable molecular entities. This section introduces the reader in both known and expected patterns of fragmentation for carbon dioxide, but also less common ones to be investigated.

For fragmentation, a good initiating mechanism is electronic excitation at the core ionization thresholds (e.g. C1s and O1s for CO_2). Going over this barrier one reaches the ionized state, in which the excess energy is most often taken care of by emission of an Auger electron, thus forming doubly charged parent ion. Triply charged ions are also possible, due to double Auger decay or, in some cases by a cascade of Auger decays, but indeed, the primary de-excitation pathways produce singly and doubly charged ions, below and above the ionization threshold, respectively [16].

Fragmentation of carbon dioxide after core excitations has been studied, among others, by Öhrwall *et al* [17] and their results are reviewed in the following, not least to provide some motivation for present experiments. The most probable reaction producing ions after core-level electron excitation is the resonant Auger decay:

$$\mathrm{CO_2}^* \rightarrow \mathrm{CO_2}^+ + \mathrm{e}_{\mathrm{resA}}$$

Furthermore, there is the possibility that the excited molecule emits a photon via fluorescence, before the dissociation. Such event is shown below, CO_2^* and CO_2^{**} representing initial excited state and the (still excited) state after the photon emission, respectively.

$\mathrm{CO}_2^* \rightarrow \mathrm{CO}_2^{**} + h \nu$

In the case of core ionization, the Auger decay dominates:

$$\mathrm{CO_2}^+ \rightarrow \mathrm{CO_2}^{++} + \mathrm{e}_{\mathrm{A}}$$

thus forming the doubly-charged parent ion, CO_2^{++} . From these parent ions, singly or doubly charged, the fragmentation usually starts,

yielding C⁺, O⁺, CO⁺ and CO₂⁺ [17] [18] [19], but also negatively charged fragments, such as C⁻ and O⁻, can appear [17].

I shall now construct the probable dissociation pathways, taking into account the previously presented steps. As known, innershell photoionization is followed by a core-hole decay and emission of an Auger electron. This process creates usually a highly unstable, doubly-charged parent ion. Due to electrostatic repulsion, the molecule can undergo Coulomb explosion, in which they break into energetic, singly charged fragments [20]. This process is illustrated in Fig. 2.11. Two of the probable pathways forming singly-charged cations following Auger decay are shown here:

$$\mathrm{CO}_2^{++} \rightarrow \mathrm{O}^+ + \mathrm{C}^+ + \mathrm{O}$$
 and

 ${\rm CO_2}^{++} \to {\rm O}^+ + {\rm C} + {\rm O}^+.$

Doubly charged ion fragments are also a possibility at, and especially above the O1s edge (C⁺⁺ and O⁺⁺).

Furthermore, anion fragments can also form following core excitation or ionization, thus they are included in the possible fragmentation pathways. If one takes into account core excitations (below the O1s ionization threshold), negative ions are created by ion-pair formation from CO_2^+ parent ion when it fragments into a CO^{++} dication [17], such as:

$$\mathrm{CO}_2^+ \rightarrow \mathrm{CO}^{++} + \mathrm{O}^-$$
 and

 $\rightarrow \mathrm{C}^{+} + \mathrm{O}^{+} + \mathrm{O}^{-}.$

where CO⁺⁺ breaks into two singly charged cations. In addition, anions are also created following ion-pair formation from a neutral excited and unstable CO fragment, yielding the following pathways:

$$CO_2^+ \rightarrow CO + O^+,$$

 $\rightarrow C^+ + O^- + O^+, \text{ and}$
 $\rightarrow C^- + O^+ + O^+.$

Above the O1s ionization potential, where Auger decay is most likely (thus forming the CO_2^{++} parent ion), anions can also be formed along with singly or doubly charged cations, and some possible pathways are given below:

$${\rm CO_2}^{++} \rightarrow {\rm C}^{++} + {\rm O}^- + {\rm O}^+$$

 ${\rm CO_2}^{++} \rightarrow {\rm O}^{++} + {\rm C}^- + {\rm O}^+.$

Again, the information from both the negative and positive ions allows to separate these fragmentation paths and, they will indeed be taken into account when identifying the molecular fragments in the recorded time-of-flight mass spectra, to be presented in the following sections.

Furthermore, there is a possibility for electron recapture events, at the onset of Auger decay just above the ionization threshold:

$$[\operatorname{CO}_2 + h\nu] \to \operatorname{CO}_2^+(1s^{-1}) + e_{\mathrm{ph}}$$
$$\to \operatorname{CO}_2^{++} + e_{\mathrm{ph}} + e_{\mathrm{A}}$$

with $1s^{-1}$ illustrating that the molecular parent ion has a core hole on the O1s orbital and the second line showing the Auger decay. From here, CO₂⁺⁺ can recapture a slow photoelectron and then dissociate as follows:

$$\mathrm{CO}_2^{+*} \rightarrow \mathrm{CO}^+ + \mathrm{O}^*$$

with O^* representing the fragment that received the recaptured photoelectron after dissociation. From here, through the fragmentation of CO^+ cation, the pathways can become:

$$[CO^+ + O^*] \rightarrow C^+ + O + O^*$$
, or $C + O^+ + O^*$

As stated in [21], these fragments can be metastable, in which case they have a lifetime of microseconds, or fully stable but, as present setup is not suitable for detecting photons typically emitted in their decay, they shall not be explored further.

The fragmentation pathways considered so far assume there is no external processes such as gas pressure dependency of electron reattachment to a neutral fragment or of electron capture by positive fragments. This issue was briefly discussed in [17] [22] and suggested that pressures in the range of $1*10^{-5}$ mbar were low enough to ensure single-collision conditions. Even though our pressures read values around $4*10^{-7}$ mbar, the pressure can be higher at the exit of the gas needle, however less than two orders of magnitude [23], which means that the single collision condition was met well in the present measurements.

This work aims to experimentally investigate the dissociation dynamics of CO_2 by using time of flight spectroscopy, method described in the following section, and especially emphasizing the additional information reachable with negative ion measurements.



Figure 2.11: Example of a Coulomb explosion of carbon dioxide forming the unstable CO_2^{++} doubly-charged cation, with resulting CO^+/O^+ ion pair.

CHAPTER 3

METHODS AND INSTRUMENTATION

In order to produce core level excited and ionized states for the carbon dioxide molecule, one needs a high-flux soft X-ray radiation source with narrow spectral width. This is attainable in practice at a synchrotron radiation facility. The high-speed electrons in the storage ring (synchrotron) are used to produce light which is then extracted and fed to the experiment through a beamline.

The measurements for this work were carried at *Elettra* synchrotron radiation source (Trieste, Italy) at the *Gas Phase Beamline* (described in Ch. 3.2), using two ion time-of-flight (TOF) mass spectrometers. This chapter describes the instrumentation methods used to acquire our data.

3.1 Synchrotron radiation

Core-excitation of the gas-phase carbon dioxide molecule is done in the presence of X-ray light at more than ca. 300 eV photon energy. Furthermore, good energy resolution and high flux are required for good experimental data acquisition. These conditions are achievable at modern synchrotron radiation facilities.

A synchrotron is a particle accelerator designed, in this case, to store electrons for light production. It consists of straight sections, bending magnets, acceleration cavities and insertion devices (undulators and wigglers), electrons traveling at all times in a vacuum chamber (ultra high vacuum conditions, otherwise they would have a very short free path).

Synchrotron light is generated when charged particles are accelerated perpendicularly to the velocity vector by magnetic fields. It was firstly created in bending magnets (1947 [24]) and it was considered a "parasitic" event as it drained the beam of energy with every turn. Nowadays, synchrotrons are built solely for light generation as it exhibits outstanding characteristics.



Figure 3.1: Schematic of light produced in a bending magnet.

Light is extracted from bending magnets or insertion devices such as undulators and wigglers. A schematic of an undulator is shown in Figure 3.2. It consists of an array of permanent magnets which are laid over and under the vacuum chamber, with adjustable gap (for energy tuning). The magnets are arranged such that the resulting magnetic field vector has an alternating direction. Electrons feel the magnetic field and oscillate accordingly, thus emitting a photon with each oscillation.



Figure 3.2: Schematic of an undulator layout, with red and blue being the magnetic poles (with the field direction indicated by arrows). The electron beam is drawn in green and the yellow arrows at each bend represent the synchrotron radiation being produced.

Photons are emitted in the direction of electron propagation and the small electron bunch is the actual source of emission. Therefore, the resulting beam size and divergence are considerably smaller than conventional X-ray sources. As polarization is linked to the motion of electrons, it is also well defined (e.g. linearly polarized light due to the fact that the electron oscillation occurs in one plane). As the gap between the magnetic arrays is adjustable there is a wide range of tunability in photon energy (or its wavelength λ); the relation governing this is called the undulator equation [25]:

$$\lambda = \frac{\lambda_u}{2n\gamma^2} \left(1 + \frac{K^2}{2} + \gamma^2 \theta^2\right) \tag{3.1}$$

where the K factor is $K = e B_0 \lambda_u / 2\pi m c$, $\gamma = \frac{1}{\sqrt{1-\beta^2}}$ the Lorentz factor, θ the angle relative to the center of the radiation cone (usually very small), n the harmonic and λ_u the undulator period. Thus, by adjusting the gap between the magnets, one varies the magnetic field strength and the K factor implicitly, allowing to tune to the desired wavelength of light and its higher harmonics.

An important quality measure for the light source is called *brilliance* and it is defined as [24]:

Brilliance =
$$\frac{\text{photons}}{\text{second}*\text{mrad}^2*\text{mm}^2*0.1\%\text{BW}}$$
 (3.2)

taking into account the photon flux (number of photons/sec), the angular divergence, source cross-section and number of photons in 0.1% bandwidth of the selected central wavelength. For a higher flux at high photon energies, one would close the undulator gap to the minimum value: although the fundamental wavelength gets longer (smaller photon energy) the high energy part of the undulator spectrum is fairly smooth and intense, resembling that of a wiggler.

3.2 Gas Phase Beamline

Our measurements were carried at the *Gas Phase Photoemission* beamline at Elettra Synchrotron, Italy, in February 2016. It is a beamline designed for gaseous samples, to perform photo-emission, photo-absorption and coincidence measurements, the latter being of interest for us.

The light source is a 36 period undulator divided into 3 sections of 12 with a λ_U =12.5 cm, the maximum K factor value K=5.3 and B_{max} =0.456 T [26]. It is capable of providing light with energies between 13-900 eV.

A switching mirror and a pre-focusing mirror ensure that the photon beam from the undulator is focused at the entrance slit of the monochromator. Then, after the wavelength dispersing grating (and plane mirror coupled to the grating motion), the bandwidth of dispersed radiation is set with the exit slit. After that, the narrow bandwidth beam is refocused by Kirkpatcrick-Baez pair, vertical and horizontal refocusing mirrors, thus guaranteeing a focused, small spotsize at the experimental stations. A schematic of the optical layout is illustrated in Figure 3.3.



Figure 3.3: A schematic of the Gas Phase Photoemission beamline optical layout.

The Variable Angle Spherical Grating Monochromator (VASGM) allows for a resolving power of over 10.000 over the whole energy range by using 5 gratings to select from, depending on the desired energy range.

All this provides high photon flux and good resolving power (>10.000 over the whole energy range [27] [28]). The spot-size at the end station is relatively small (200 $\mu m \ge 200 \mu m$). However, due to refocusing solution, the end station is 1.762 m above the floor level, and the beam has an angle of 4° relative to the floor.

3.3 Ion Time-of-Flight spectrometer

A commonly used method for analyzing ionic fragments is by the use of ion time-of-flight mass spectroscopy, which differentiates between the fragments by considering their mass-to-charge ratio M/q. A major improvement in TOF instruments, so-called space focusing, was introduced by Wiley and McLaren [29]. Such mass spectrometers have good mass resolution and, in other words, the ability to differentiate small mass differences. A typical layout of such a device is shown in Figure 3.4.

Figure 3.4 illustrates the constituent parts of a TOF spectrometer: extraction region, acceleration region, field free region and detector. The extraction region consists of a space of length L where an extraction voltage V is applied between two grids, pusher and extractor [30]. This is the location where negative or positive fragments, depending on the polarity of the grids, are pushed towards the acceler-



Figure 3.4: A schematic layout of a time-of-flight spectrometer.

ation region. In the process of dissociation, the resulting fragments will have an initial kinetic energy therefore, the extraction voltage is carefully chosen so as to ensure a high transmission/acceptance angle, in practice the ability to "collect" ions and send them towards the detector before they have time to escape the extraction region due to initial kinetic energy - this matter will be given more attention in the following, especially how it is related to present instrument. The acceleration region provides a final increase in kinetic energy of the particles and the field free region (or drift-tube) leads to the detector, ensuring longer flight times and better separation of the fragments with different velocities for detection resolution. The total flight duration of an ion will be the sum of the times the fragment spends in each part of the spectrometer:

$$T = T_e + T_a + T_D \tag{3.3}$$

Measuring this time provides the information about charge to mass ratio M/q. Knowing the system parameters (e.g. L, D, and V) one can simulate flight times for certain fragments in the device, thus allowing for identification of ions in spectra.

The device used for our measurements was a tandem time-offlight ion spectrometer. It consists of two TOF spectrometers used to detect positive and negative fragments in coincidence by soft X-ray excitation. Instrument is fully described by Stråhlman *et al* [23] and a schematic layout is depicted in Figure 3.7.

The negative-ion spectrometer was designed to work with the previously built positive-ion spectrometer [31] but also independently as a stand-alone instrument. It consists of a 15 mm extraction region, a 5 mm long acceleration region and a drift tube of 320 mm. The voltages applied for these measurements were ± 217 V at the ex-



Figure 3.5: Positive and negative acceptance angles for H^- ions measured with respect to the perpendicular direction on the spectrometer axis, for the negative ion spectrometer.

traction plates, 1985 V over the MCP detector and +2000 V at the drift tube.

Due to the fact that negative ions are considerably less abundant than positive fragments, the corresponding spectrometer was built to have as high transmission as possible, so as to compensate for the low yield of negative ions. In the design phase, the goal was to have a large detector (for high acceptance angle) and as short as possible drift tube while still preserving the required mass resolution. As cation fragments are plenty, the conditions for the positive ion spectrometer were not so stringent. I have performed simulations in SIMION software to quantify the acceptance of the instrument and the results are shown in Figure 3.5.

Given that lighter ions tend to have higher kinetic energies [23] and, even at the same kinetic energy, a lighter ion would have greater velocity (thus a higher probability of hitting the outer walls of the spectrometer) the simulations were carried using negative hydrogen ions H^- with initial kinetic energies ranging between 0 and 20 eV. The results were promising due to the fact that all the ions with initial kinetic energies up to 12 eV were collected at the detector.

Simulations were also performed for the positive-ion spectrom-



Figure 3.6: Time-of-flight difference spectrum recorded at two different photon energies for low pressure carbon dioxide gas. Feature assigned with (*) is unknown, as it does not match any time-difference for CO_2 ionic fragments.

eter, using H^+ positive fragment, due to the fact that it is the lightest possible positive ion, thus most prone to hitting the outer walls of the instrument; it was found to be capable to record all ions with velocities perpendicular to its axis and initial kinetic energies up to 5 eV. Although it has considerably lower transmission than the negativeion spectrometer, the higher abundance of positive fragments compensates for this. Indeed, the instrument was found to perform well in the initial experiments [31] and in several coincidence studies, such as [23].

3.4 Coincidence measurements

A coincidence measurement is a method used to determine whether two or more events occurred within a given time frame or, several detections arose from the same event. The start signal (start of timing electronics) is provided, in this case, by the detection of a negative fragment. The stop signal is given by the positive ion detection but that is actually delayed to make sure that even the signal from the lightest positive ion comes to the measuring electronics after any possible negative ion start. If there is no stop signal in that time duration, the event is ruled out in later analysis. Detection of two consecutive negative fragments (i.e. two start signals) also restarts the measurement. Even though this scheme is highly effective for two fragment coincidences (e.g. NIPICO - Negative Ion Positive Ion Coincidence), three or four simultaneous coincidences are not possible due to the delay unit used, being able to pass only the first pulse arriving to it. This limitation can be circumvented by recording all the events at both detectors and using computer software to find coincidences after the data collection is finished; this became actually the main method for measuring coincidence events. In this continuous acquisition mode, the start signal is given by a pulse generator operating at 10 Hz, and the signals from both detectors are fed into the TDC unit (Time to Digital Converter - ACAM Messelectronic) after pre-amplifier/constant fraction discriminator stage. The TDC unit used in this case has a time resolution of 80 ps [31]. The simplified schematic of the aforementioned setup is depicted in Fig. 3.8.





As negative ions are not as abundant as positive fragments, this also means that they are not as abundant as electrons either (positive ion formation is often connected to direct or indirect photoionization). Taking into account that the electrons travel in the same direction as the negative ions, they would saturate the corresponding detector. In order to avoid that, a deflecting magnetic field was introduced between the source region and the negative ion detector. This was achieved by mounting two permanent neodymium magnets on the drift tube of the negative ion spectrometer (outside the vacuum chamber), thus ensuring the deflection of unwanted electrons whilst not affecting the flight times of even the lightest negative ion fragments [23] (simulations also performed by the author to confirm this matter). A typical spectrum obtained is illustrated in Figure 3.6. Several ion coincidences are marked next to their corresponding peaks.



Figure 3.7: A schematic layout of the tandem time-of-flight ion spectrometer. Picture from Christian Stråhlman.

CHAPTER 4

ANALYSIS

The results presented here were recorded using an ACAM card in continuous acquisition mode (as described in Chapter 3.4), thus ensuring the possibility of detecting multiple coincidences. The recorded spectra were imported and analyzed with Igor software. This section describes the analysis and interpretation of our data.

4.1 Anion-cation coincidence spectra

As explained in Chapter 3, the data consists of the number of events (normalized to experimental conditions) plotted against time difference between the detected signals at the two spectrometers. For this data, the timespan allowed for finding coincidences was 12000 ns and the zero was set at 5000 ns in the analysis. The data treatment was such that a time-stamp of a negative fragment was regarded as a start signal. From that, the presence of a positive fragment is checked within the time window and the time difference between these two (or more) time-stamps is calculated and saved, thus explaining the occurrence of the coincidence events. A result of analysis of coincidences recorded at 535 and 538.79 eV (O1s edge core-excitations) showing the identified ion-pairs is illustrated in Fig. 4.1. Even though there was a magnetic field for electron deflection, coincidences between electrons and positive ions are still observed due to the high abundance of the latter (the magnetic field deflects most electrons to avoid detector saturation, but a small fraction still reach the detector).

As the measurements were done in continuous acquisition mode, which explains why the recorded ion coincidences can show below and above the zero-point, 5000 ns: there could be a case of a positive fragment hitting its detector before the negative ion start, and still resulting from the real event. For example, if one considers the coincidence pair C^{++}/O^{-} , the start signal was the detection of O^{-} .



Figure 4.1: Coincidence spectrum for CO_2 molecule core-excited with 535 eV (blue) and 538.79 (red) radiation. Narrow peak (assigned *) just below 4000 ns appeared in all measurements, including valence excitations at 18 eV, thus was attributed to noise/malfunction in the device. Structure marked with (**) does not point to any real time difference. Acquisition time was 120 minutes for each photon energy.

Provided that C^{++} is doubly charged and taking into account the mass to charge ratio (M/q), C^{++} has 6 and O⁻ 16, in absolute values, C^{++} will fly and reach the detector much faster than O⁻, considering the positive and negative voltages applied are somewhat similar.

On the other hand, in the case of positive ion/electron coincidence, one can see that they tend to be further in the "positive zone" (i.e. far above 5000 ns time difference; this is the reason why the zeropoint is asymmetrically in the time window, to allow for a wider range to detect PEPICO events). This is due to the fact that electrons are very light, so they will reach the detector considerably faster; e.g. the CO^+/e^- coincidence has a time difference of over 3000 ns due to the fact that CO^+ has M/q = 28 and the electron time of flight can be though of as almost instantaneous. The lighter the positive fragment (or lower mass to charge ratio) the shorter flight time difference they have, relative to electrons.

As can be seen in Fig. 4.1, there are positive, negative and doubly charged fragments present. This is in good agreement with the non-coincidence study performed by Öhrwall *et al* [17] for the core-excitation at the O1s edge, but provides complementary information directly about the probability of various fragmentation pathways, as ions are measured in coincidence with each other.

4.1.1 Core-level photon energies - O1s edge

Singly-charged fragments in coincidence

The experiment described above is repeated for many photon energies in order to find out how fragmentation develops at coreexcitations and after core-ionization. For further interpretation, the intensities of the coinciding ion pairs as a function of photon energy are plotted and analyzed. Even though the intensity is displayed in arbitrary units, there is normalization between all the measurements, as they were analyzed in the same manner. The NIPICO events for singly charged positive ions created around the O1s ionization threshold of 541.2 eV [1] are shown in Fig. 4.2.



Figure 4.2: Singly-charged positive fragments in coincidence with negative ions as a function of photon energy at O1s edge. Dotted lines are added to guide the eye; the vertical bars show the excitation energies for O1s to 3p, 4s and 4p orbitals, and the O1s ionization potential in CO_2 .

Such a plot provides valuable insights about the dissociation channels and their relative probability across the photon energy range. From Fig. 4.2, one can observe that the most favorable ionic fragment pairs are: C^+/O^- and O^+/O^- , revealing considerably higher

intensity (directly correlated to abundance) than CO⁺ or O₂⁺ in coincidence with any anion; the weakest, but still observable ion-pair signal includes C- ion. As presented in Ch. 2.6.3, above IP, normal Auger decay is most likely, thus producing CO₂⁺⁺ doubly-charged parent ion. However, there is the possibility of double excitations where the incident photon produces a O1s $\rightarrow \pi^*$ excitation and simultaneously a valence excitation to an unoccupied orbital; the decay in this case can be resonant Auger thus resulting in CO₂⁺ and explaining the increase in counts at roughly 555 eV.

Although not shown here, present measurements at valence-level excitations reveal NIPICO cases only with O⁻ as the anion, rather than C⁻. This is in agreement with the results from [17]; they concluded that C⁻ was not observed below the O1s edge; coincidences such as O_2^+/C^- and O⁺/C⁻ were not found at the vicinity of C1s ionization threshold.

Furthermore, PEPICO events were given the same treatment and the results are plotted in Fig. 4.3. An immediate observation is the



Figure 4.3: Singly-charged positive fragments in coincidence with electrons as a function of photon energy at O1s edge.

higher number of cation/electron coincidences (PEPICO) above IP. After IP, the doubly-charged CO_2^{++} parent ion can fragment to two

singly-charged cations, meaning that for each electron there are two possible cations to be detected in coincidence. Another matter is the low probability for CO_2^+ production at high photon energies, quite different to valence ionization where it is the most likely fragment. This is actually a good demonstration related to the cross-section result presented in Chapter 2.2: as the valence ionization cross section decreases towards higher photon energies, it is clear that the corresponding fragmentation channel almost disappears as the energy increases, having close to zero intensity at O1s core-level excitation. This is due to the valence ionization cross-section values decreasing as the energy reaches higher values [32] and the fact that core level ionization, and excitation, also bring the molecule into a very unstable state with energy clearly higher than the double ionization energy. Here the inner shell electrons have an increasing photoabsorption cross-section, thus explaining the low probability for ionic fragments produced via valence ionization at the O1s edge; they are still detectable but exhibit the behavior of a slowly decreasing background, as already seen in [17].

Although it is easy to notice $O1s \rightarrow 3p$ and $O1s \rightarrow 4p$ excitations, the electron/positive ion yields are relatively strong at $O1s \rightarrow \pi^*$ resonance too. Below IP, the most likely decay mechanism, forming CO_2^+ parent ion, is resonant Auger and the resulting energetic electrons had the highest probability of bypassing the deflecting magnetic field (see Chapter 3.3), thus explaining their high intensity in a PEPICO plot, in agreement to [17]. Furthermore, it is easy to notice the $O1s \rightarrow 4p$ shoulder at 539.96 eV [2], where there is a peak in abundance for most of the positive fragments, also suggested in [17].

Doubly-charged fragments in coincidence with anions or electrons

Doubly-charged cations were also found in coincidence with anions and they are shown in Fig. 4.4. The $O1s \rightarrow \pi^*$ resonance shows nonzero intensity, but one can clearly notice the $O1s \rightarrow 4s$, $O1s \rightarrow 3p$ (538.53 eV [2]) and $O1s \rightarrow 4p$ (540.3 eV [2]) absorption edges for the CO_2 molecule as peaks of higher intensity.



Figure 4.4: Doubly-charged positive fragments in coincidence with negative ions as a function of photon energy at O1s edge.

As seen in Fig. 4.4, there is considerable intensity of this type of pairs above IP. Even though the negative ions are not as abundant as positive ions, the high transmission of the negative ion spectrometer allowed for their detection. Another valuable observation to be made in this case is the relative abundance between coincidences including singly and doubly-charged cations. It is quite noticeable that the signal coming from singly-charged positive ions is higher than for doubly-charged cations. This is due to the fact that the fragmentation of such a dication can occur before the detection (almost immediately in the extraction region, or later on in the accelerating region or drift tube of the spectrometer), thus reducing its signal strength.

Last but not least, PEPICO events including doubly-charged cations were also extracted and the events plotted as a function of photon energy are presented in Fig. 4.5. One notices that the intensity for these events is roughly double than that for NIPICO events with doubly-charged positive ions, even though they are the same cationic fragments. This is expected to be due to the fact that electrons are much more abundant than negative ions and, even though there were measurements taken with the deflecting magnetic field (see Chapter 3.3) adjusted in such a way that only a small fraction



of electrons was able to go through, coincidences with the latter are more probable than with anions.

Figure 4.5: Doubly-charged positive fragments in coincidence with electrons as a function of photon energy at O1s edge.

The $O1s \rightarrow \pi^*$, $O1s \rightarrow 4s$ and $O1s \rightarrow 4p$ features show intensity in this case. After the ionization potential of 541.2 eV [1], doubly-charged states are very likely to be produced by Auger decay, and this can be seen in Fig. 4.5. However, as anions are not expected in as high abundance as dications, this process is more obvious in the PEPICO plots, also showing the usefulness of having electrons at the negative ion detector. Furthermore, electron coincidences can offer information about the parent ion: in the case of a doubly-charged cation found in coincidence with electron, the parent ion can be doubly-charged, whereas for dication/anion events, the molecular parent ion is singly-charged. They are nevertheless noticed in NIPICO events too, due to the high transmission of our instrument.

Such an analysis is already found helpful when compared to just measuring ion yields: aside from seeing which ions are present, one also gets a more detailed view of the fragmentation process, as it is possible to identify which ions (fragments) originate from the same event. However, a more complete analysis, including multiple coincidences, is presented in the following.

4.2 Coincidence results including multiple positive fragments

So far, single coincidences were investigated only and the possible fragments originating from the same event were found in different abundances across the photon energy range studied here. However, for a triatomic molecule that is not a very complete analysis. To improve that, one needs to find which two or more coincidences originate from the same event. This section describes the analysis tool to do so and presents the results found in these measurements.



Figure 4.6: Diagonal map of coincidences for the CO_2 molecule with several events and their intensities encircled in red, at 50 eV excitation. Scale chosen to show region for e-/cation coincidences.

In order to find the coincidences that originate from the same event, one plots two time difference spectra and related data as shown in Fig. 4.6 and obtains a diagonal map of scattered points. This kind of plot tells what the first observed cation was, in coincidence with a negative particle and, the second axis reveals another observed cation with the same negative particle as trigger. Here, the data is taken at 50 eV photon energy; this low excitation energy was used mainly for instrument tests but it also provides reference data to compare with at core excitation energies, and the following interpretation of results is used here as an example. Where coincidences occur, there is a higher number of points, as can be seen in Fig. 4.6 in the encircled areas. On a closer look, one notices how the multitude of data points tends to form a tilted pattern of a certain slope. This indicates the presence of momentum correlation between the produced fragments and, analyzing the position, length and width provides information regarding the masses of the two fragments and the magnitude of the released kinetic energy both to the ions and neutral fragments, see, e.g. [33]. However, this work shall restrain to identifying the dissociation pathways, leaving the aforementioned analysis for a future, more complex study.

Seeing that the 50 eV photon energy used for recording data presented in Fig. 4.6 is well above the double IP of CO_2 (37.2 eV[34]), the molecule can become doubly ionized:

$$[CO_2 + h\nu] \rightarrow CO_2^{++} + 2e_{ph}$$

From this state, the doubly-charged parent ion can fragment to cations, and data shown in Fig. 4.2 can be explained by the following fragmentation pathways:

$$CO_2^{++} \rightarrow CO^+ + O^+$$
,

 $\text{CO}_2^{++} \rightarrow \text{O}^+ + \text{O}^+ + \text{C}$ and

 $CO_2^{++} \rightarrow O^+ + C^+ + O.$

Although not shown in Fig. 4.2, the data also points to direct ionpair formation considering that O^- anion was observed too, namely:

 ${\rm CO_2}^+ \rightarrow {\rm C}^+ + {\rm O}^+ + {\rm O}^-$

4.2.1 Singly-charged fragments in coincidence with anions or electrons

Now, moving to core-level excitation energies, PEPIPICO and NIPIPICO events for singly-charged positive ions at O1s edge are illustrated in Fig. 4.7. The data plotted here represents the summation of all the counts for each dissociation channel over the whole photon energy range (O1s edge as illustrated in previous plots). Due to poor statistics, the normalized counts as a function of energy for each channel are not presented here.

These present the observed channels of molecular fragmentation at this photon energy range and the results point to the same dissociation pathways here, as shown in PEPIPICO at valence-level energies:

 $\mathrm{CO_2}^{++} \rightarrow \mathrm{CO}^+ + \mathrm{O}^+,$

 $\text{CO}_2^{++} \rightarrow \text{C}^+ + \text{O}^+ + \text{O}$ and

 $CO_2^{++} \to O^+ + O^+ + C.$

It is highly likely that the second and third pathways presented above are produced via an intermediate CO⁺ fragment, yielding either C⁺/O or C/O⁺ pairs.



Figure 4.7: Multiple coincidences for singly-charged cations with anions and electrons.

Less abundant NIPIPICO events were also searched for at this region and they are also plotted in Fig. 4.7; the probability for these channels is about one fourth of that for the PEPIPICO events. For this case the results suggest the following fragmentation pathways:

 $\mathrm{CO_2}^+ \rightarrow \mathrm{C}^+ + \mathrm{O}^+ + \mathrm{O}^-$ and

 $\mathrm{CO_2}^+ \rightarrow \mathrm{O}^+ + \mathrm{O}^+ + \mathrm{C}^-.$

4.2.2 Doubly-charged fragments in coincidence

Multiple coincidences involving doubly-charged cations were also explored at core-level excitation energies in both NIPIPICO and PEPIPICO events and the results are illustrated in Fig. 4.8. The observed dissociation pathways including doubly-charged cations in coincidence with anions are:

$${\rm CO_2}^{++} \rightarrow {\rm C}^{++} + {\rm O}^+ + {\rm O}^-,$$

 $\mathrm{CO_2}^{++} \rightarrow \mathrm{O}^{++} + \mathrm{C}^+ + \mathrm{O}^-$ and

 $CO_2^{++} \rightarrow O^{++} + O^+ + C^-.$



Figure 4.8: Multiple coincidences for doubly-charged cations with anions and electrons.

It is however obvious that the probability for the carbon dioxide molecule to form dissociation pathways consisting of doublycharged cations is considerably lower than the case of singly-charged fragments.

Furthermore, PEPIPICO events including doubly-charged cations were also considered as can be seen in Fig. 4.8. The relative strength of these fragmentation patterns is roughly similar to the aforementioned NIPIPICO case. This is due to the fact that, even

though they were identified in different coincidences (NIPIPICO and PEPIPICO), they can actually represent the same dataset. For example, $C^{++}/O^+/O^-$ NIPIPICO event and $C^{++}/e^-/O^+$ PEPIPICO event can follow form the same dissociation channel $C^{++}/O^+/O^-$, solely the analysis approach is different.

It must be noted that in producing a singly-charged cationic fragment, metastable neutral states can be achieved via the process of electron recapture: close to the ionization edge, at the onset of Auger decay [17], it results in a fast Auger electron and a much slower photoelectron. The latter can be recaptured (as explained in Ch. 2.6.3) and, following dissociation, form a metastable excited neutral state (atom), or even a negative ion therefore, the pathways could be:

 ${\rm CO_2}^{+*} \rightarrow {\rm C}^+ + {\rm O} + {\rm O}^*$,

 ${\rm CO_2}^{+*} \to {\rm O}^+ + {\rm C}^+ + {\rm O}^{-*},$

 $CO_2^{+*} \rightarrow O^+ + O^+ + C^{-*}$ and

 ${\rm CO_2}^{+*} \to {\rm CO}^{++} + {\rm O}^{-*}.$

Even though the starting parent ion CO_2^{++} was indeed doublycharged, due to recapture of the slow photoelectron, it becomes highly likely for the dissociation pathways to yield only one singlycharged cationic fragment; this is something that cannot be observed with present setup.

To sum up, the CO_2 molecule and its dissociation dynamics were studied both at valence-level excitation energies and at O1s edge. As expected, both singly-charged and doubly-charged cations were extracted and anions were recorded. The conclusions that arose from the recorded and analyzed data are dealt with in the following chapter.

CHAPTER 5

DISCUSSION AND CONCLUSIONS

The dissociation pathways of CO_2 were studied, both at low excitation energies (close to valence ionization level) and especially corelevel excitations (around the O1s ionization threshold) and the results have been reported in the previous section. Both positive and negative fragments were identified and associated with the proposed fragmentation channels of varying strengths, as shall further be discussed in the following.

5.1 Discussion

At valence level excitation energies, the strongest fragment seen is CO_2 in coincidence with an electron, corresponding to photoionization where the parent ion does not fragment; the pathway is:

 $\text{CO}_2 + h \nu \rightarrow \text{CO}_2^+ + \text{e}_{\text{ph}}$

This channel becomes weaker towards higher photon energies, as the cross-section for valence ionization decreases. Besides the strongest channel presented above, other fragments were observed. For photon energies above 37.2 eV (double IP for CO_2 [34]) the molecule can become doubly photoionized:

$$\text{CO}_2 + h \nu \rightarrow \text{CO}_2^{++} + 2 \text{e}_{\text{ph}}$$

The doubly-charged parent ion usually dissociates yielding CO⁺/O⁺:

$$\mathrm{CO_2}^{++} \rightarrow \mathrm{CO}^+ + \mathrm{O}^+$$

with CO⁺ fragmenting further, thus forming the following pathways:

$$\mathrm{CO}^+ + \mathrm{O}^+ \rightarrow \mathrm{O}^+ + \mathrm{O}^+ + \mathrm{C}$$
 and

 $\mathrm{CO}^+ + \mathrm{O}^+ \rightarrow \mathrm{O}^+ + \mathrm{C}^+ + \mathrm{O}.$

Furthermore, O^- anion was observed [17] at valence level photon energies (below double photoionization) in $C^+/O^+/O^-$ channel. The anion was produced following ion-pair formation, likely via an intermediary neutral excited fragment CO:

 $\mathrm{CO_2}^+ \rightarrow \mathrm{CO} + \mathrm{O}^+$

 $[CO + O^+] \rightarrow C^+ + O^- + O^+.$

Moving now to O1s $\rightarrow \pi^*$ excitations, the presence of O_2^+/C^- channel is observed. It was proposed [17] that O_2^+ fragment appears at this photon energy due to overlapping of 3s Rydberg orbitals. The conclusions to be drawn are, on one hand, the earlier predictions and results [17] are confirmed and, on the other hand, the instrument works very well and has a high sensitivity for the detection of very weak channels (as seen in Fig. 4.2, O_2^+/C^- channel shows a relatively weak intensity).

Here, the core excited molecule is likely to form a singly-charged parent ion via resonant Auger process:

 $\text{CO}_2 + h \nu \rightarrow \text{CO}_2^+ + \text{e}_{\text{resA}}$

and the most probable dissociation channels include singly-charged positive ions in coincidence with anions, such as:

 $\text{CO}_2^+ \rightarrow \text{C}^+ + \text{O}^- + \text{O}^+$ and

 $\mathrm{CO_2}^+ \rightarrow \mathrm{C}^- + \mathrm{O}^+ + \mathrm{O}^+.$

Weaker, but still possible channels are doubly-charged positive ions in coincidence with negative ions such as C^{++} , O^{++} and also fragments like CO^{++} . The latter tend to be very unstable but we have seen them in coincidence with anions as follows:

 $\mathrm{CO_2}^+ \rightarrow \mathrm{CO}^{++} + \mathrm{O}^-$

Above O1s ionization threshold, the most probable event after photoionization is Auger decay. As has been seen in Chapter 4.1.2, normal Auger process produced CO_2^{++} which is expected to decay as illustrated by the following [11]:

$$CO_2^{++} \rightarrow CO^+ + O^+ \rightarrow O^+ + O^+ + C$$
 or $O^+ + O + C^+$

which yields neutral atomic fragments (O and C).

Anions were also identified above the O1s IP (C^- and O^-) and their presence was expected to be due to recapture processes, but our data does not point to that. The likelihood of anion production at these energies comes from valence and core double excitations.

However, above IP, a strong signal came from doubly-charged cationic fragments in coincidence with anions and this is easiest to notice in Fig. 4.4. The dissociation pathways (additionally to the ones already presented) with anions are:

$$CO_2^+ \rightarrow C^- + O^+ + O^+,$$

 $CO_2^+ \rightarrow C^{++} + O^+ + O^-,$

 $\mathrm{CO_2}^{++} \rightarrow \mathrm{O}^{++} + \mathrm{C}^+ + \mathrm{O}^-$ and

 $CO_2^{++} \rightarrow O^{++} + O^+ + C^-.$

Triply-charged states are also a possibility, they can be created in a double Auger decay. [11]. The most likely dissociation channels for a triply-charged CO_2^{+++} are C^{++}/O^+ or C^+/O^{++} [17] which we have found. However, statistically more reliable results are required to safely argue the presence of such fragment.

5.2 Conclusions

This work discusses the photoionization of carbon dioxide molecule at core-level photon energies, with a focus on studying the dissociation dynamics. There has been considerable effort in exploring the photoionization and ion yields of CO_2 , see e.g. [17; 18; 22] all of them being non-coincidence studies. The newly developed instrument is based on coincidence detection, thus allowing to pinpoint more precisely how the negative ions are produced (i.e. their pathways). This paper confirmed earlier suggestions and offered a more complete description of the dissociation patterns.

First and foremost, the newly designed negative-ion spectrometer was found to perform very well. The high transmission together with the deflecting magnetic field allowed for the detection of very low-abundance negative ions, confirming its capabilities in negative ion/positive ion coincidence experiments.

Both anions and cations were found and identified at corelevel photon energies. Positive fragments were singly and doublycharged; triply-charged cations (CO_2^{+++}) are expected to form but due to their dissociative nature they fragment further much before they reach the detector.

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