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Single photon double valence ionization of vinyl halides

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Abstract

Using a He lamp and a magnetic bottle spectrometer we measured the single ionization potential and the double ionization potential of $C_2H_3Br$, $C_2H_3Cl$, $C_2H_4$ and recorded their spectra at a photon energy of HeII$\alpha$ and HeII$\beta$. The coincidence maps obtained from our measurements indicate that primarily direct double ionization occurs in these molecules. Due to the fact that ionization processes in this thesis involve valence electrons, we have tested the validity of an empirical equation, from which the distance of the holes created in the dication can be estimated if the values of the single and double ionization potential are known. It was found that the bond length between the carbon atoms was increased due to the repulsion of the holes created in the outermost valence orbital and our data are in agreement with theoretical predictions, but in order to verify the applicability of this empirical relation on solid grounds, ab initio quantum chemical calculations are desired.

Sammanfattning på svenska


Enkel- och dubbel-jonisationspotentialen uppmättes för $C_2H_3Br$, $C_2H_3Cl$ och $C_2H_4$ med en magnetisk flask-spectrometer. En He-lampa användes för att producera det joniserande ljuset med en fotonenenergi motsvarande HeII$\alpha$ och HeII$\beta$ emissions linjerna. De resulterande koordinenskartor från våra mätningar visar på en huvudsaklig direkt jonisationsprocess i dessa molekyler. Enkel- och dubbeljonisation av valenselektroner användes för att testa en empirisk ekvation, som gav ett approximerat värde av avståndet mellan de elektron-hål som skapades i jonisationsprocessen. Detta gav en indikation av att avståndet för bindningen mellan kol-atomerna ökade vid en jonisation av de yttersta valenselektroner, vilket stämmer överens med den teoretiska bild som ges av jonisationsprocessen. För att verifiera resultaten från denna undersökning behövs ytterligare kvant-kemiska beräkningar.
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1 Introduction

The aim of this thesis is to study the ionization processes taking place in vinyl halides, using a time of flight (TOF) coincidence spectroscopy technique, based on a magnetic bottle spectrometer, which was originally introduced by John H.D. Eland at Oxford University [1]. A vinyl halide is an alkene which has at least one halide substituent bonded on one of the carbons. Vinyl halides are frequently used as synthetic intermediates in many chemical reactions and can also be used for the synthesis of polymers and copolymers. By studying the ionization processes of these molecules we can have an insight to their electronic structure and notable progress are expected to be made both in synthesizing new polymers used for industrial applications and in the field of Quantum Chemistry. Vinyl chloride and vinyl bromide are two prominent examples of vinyl halides and are the ones studied within the framework of this thesis.

The structure of the thesis will be as follows. First we recapitulate briefly some theoretical aspects of Quantum Mechanics regarding atomic and molecular orbitals. After that we continue by introducing the concepts of Single Photo-ionization and Double Photo-ionization, which are central to this thesis work.
Before describing the actual experimental setup, we end the theory part by explaining Auger transitions, which is an alternative pathway for reaching the same final dicationic states studied in this work.

Within the description of the experimental setup, first an overview of our TOF spectrometry technique is given and then the main parts of the equipment, which are the He lamp, the magnetic bottle and the MCP detectors, are described. This section ends by explaining how the time to energy conversion is done and by explaining what a coincidence map is, since some of the results will be presented in this form.

In the subsequent chapter, our experimental results for vinyl chloride and vinyl bromide are presented. Our results are compared with the current literature and from the spectra and coincidence maps acquired we discuss possible interpretation of the ionization processes of the two molecules studied. The thesis ends with conclusions from our experiments.

2 Theoretical background

In what follows a brief recapitulation will be given of what atomic and molecular orbitals are. Then we explain the terminologies Single Photo-ionization and Double Photo-ionization. Both processes are frequently utilized in the field of charged-particle TOF experiments and it is crucial to distinguish the one from the other. We end the theoretical part by describing Auger transitions and how Auger spectra can be used for direct comparison with our experimental results.

2.1 Atomic and molecular orbitals

It is known from Quantum Mechanics and Physical Chemistry [2] that a lot of important information of microscopic systems (e.g. atoms, molecules) is contained in the wavefunction \( \Psi \) of the system. The wavefunction can be obtained by solving the Schrödinger equation:

\[
\hat{H} \Psi = E \Psi, \tag{1}
\]

where \( \hat{H} \) is the Hamiltonian of the system, given as the sum of the kinetic and potential energy operator and \( E \) denotes the energy eigenvalues of the system. Equation 1 can be solved exactly for hydrogenic-type atoms (i.e. the hydrogen atom or one electron ions) and the results can be used to describe, in good approximation, many-electron systems. In what follows we will present the solution of equation 1 for a hydrogenic atom without entering mathematical details. Those can be found in many textbooks like [2].

The Hamiltonian of a hydrogenic atom will be:

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{Ze^2}{4\pi\epsilon_0 r}, \tag{2}
\]

where the first two terms denote the kinetic energy of the electron and the nucleus respectively and the last one is the electrostatic interaction between the electron and the nucleus. If we insert equation 2 to equation 1 and apply certain mathematical techniques (transformation to spherical coordinates, variable separation) we can solve equation 1 and get the wavefunction \( \Psi \). We note that the wavefunction will be the product of a radial and an angular part (\( \Psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \)), where the first one will satisfy the radial wave equation and the second part can be expressed in terms of spherical harmonics. The solutions of equation 1, i.e. the wavefunctions, that describe one specific electron in an atom are called atomic orbitals. By solving equation 1 one can see that each atomic orbital will be described by three quantum numbers, namely \( n, l, m_l \).

The first quantum number, \( n \), is called the principal quantum number, which determines the energy level as we will shortly see. It comes from the solution for the radial part and takes the values \( n = 1, 2, \ldots \). The other two quantum numbers, \( l \) and \( m_l \) specify the angular momentum and the z-component of the angular momentum respectively. They come from the solution of the angular part and they can have the values \( l = 0, 1, \ldots n - 1 \) and \( m_l = -l, \ldots, 0, \ldots, l \) respectively. There is also a fourth quantum number which shows the spin of the electron occupying the specific \( (n, l, m_l) \) orbital, denoted by \( m_s \) and getting the values \( m_s = \pm \frac{1}{2} \).

The energy eigenvalues now can be found to be:

\[
E_n = -\frac{Z^2m_e e^4}{32\pi^2\epsilon_0^2\hbar^2n^2}. \tag{3}
\]
What one should notice in equation 3 is the minus sign which corresponds to the bound atomic states and the fact that we have discrete atomic levels which are proportional to $Z^2/n^2$, where $Z$ denotes the atomic number and $n$ is the principal quantum number. We can describe now the atomic levels in terms of the quantum numbers $n, l$. We say that the orbitals of given $n$ form a shell and those having the same $n$ but different $l$ form sub-shells in the shell. The common way to refer to the shells and sub-shells is the following:

$$
\begin{array}{c|cccc}
 n & 1 & 2 & 3 & 4 \\
 \hline
 K & L & M & N \\
 l & 0 & 1 & 2 & 3 \\
 s & p & d & f \\
\end{array}
$$

Table 1: Standard notation of shells and sub-shells depending on the values of $n, l$.

What we see in table 1 is that we assign an uppercase letter starting from K and proceeding alphabetically for each value of $n$ and the same for $l$ but now with lowercase letters and proceeding alphabetically for values $l \geq 4$. A schematic representation of energy levels in terms of $n, l$ can be seen in figure 1.

The circles in figure 1 represent the $m_l$ values. For example, a p sub-shell corresponds to $l = 1$, and there are three different $m_l$ values, $m_l = -1, 0, 1$. Regarding the Pauli exclusion principle, according to which there can’t be electrons with the same set of quantum numbers, for each value of $m_l$ we can have two electrons ($\pm \frac{1}{2}$). This implies that a s sub-shell can be filled at most by 2 electrons, a p sub-shell with 6, a d sub-shell with 10, etc. Finally, we mention that the order in which the atomic orbitals are filled with electrons follows the so-called build-up (Aufbau) principle and can be found in many Physical Chemistry textbooks.

Let us proceed now by describing briefly also the molecular electronic structure. It is known that the two main theories regarding molecular orbital structure are the Valence Bond (VB) theory and the Molecular Orbital (MO) theory. We will describe both theories briefly, starting by VB theory.

According to the VB theory, a bond is formed by the overlap of two valence atomic orbitals of two different atoms, each containing an unpaired electron. The two electrons pair their spins resulting in the formation of a bond. There are two different types of overlap which can result in the formation of sigma ($\sigma$) and pi ($\pi$) bonds. A $\sigma$ bond is formed when the overlapping orbitals have cylindrical symmetry around the internuclear axis (head to head overlap). A $\pi$ bond is formed when the orbitals overlap side by side, so the axes of the orbitals are perpendicular to the internuclear axis. The formation of $\sigma$ and $\pi$ bonds in the ethylene molecule can be seen in figure 2. Though VB theory describes the formation of bonds based on quantum mechanical arguments, it has certain weaknesses. It predicts a bond angle for the water molecule of 90°, whilst the one measured experimentally is 104.5°. An improved theory after VB is the MO theory, which is also the one frequently used up to date.

In order to introduce the MO theory, let us consider the singly-ionized hydrogen molecule $\text{H}_2^+$. The
Hamiltonian describing this molecule within the Born-Oppenheimer approximation is:

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2_e - \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{|\vec{R}_A - \vec{R}_e|} + \frac{1}{|\vec{R}_B - \vec{R}_e|} + \frac{1}{|\vec{R}_A - \vec{R}_B|} \right), \]  

(4)

where the denominators of the terms in the parentheses are the distances of the electron from the first nucleus, the distance of the electron from the second nucleus and the distance between the two nuclei. The wavefunctions obtained from equation (1) under the Hamiltonian (4) are called molecular orbitals. As it can be seen by integrating \( |\Psi|^2 \) (which is the probability density function) over the whole space, the electron does not belong to a certain atom anymore but to the entire molecule. This is an important point in MO theory and applies to every molecule. At that point we can also add that equation (1) cannot be solved analytically for atoms with many electrons (He is the simplest many-electron atom, which has only two electrons) and the same applies for molecules, so certain approximations may need to be applied.

Some important conclusions emerging from MO theory should be mentioned in the present context. First we can see that since the electron can belong to atom A and atom B the molecular orbital should be a superposition of atomic orbitals. So it can be written as:

\[ \Psi_{\pm} = N(\Phi_A \pm \Phi_B), \]  

(5)

where \( \Phi_A \) is the wavefunction of A and \( \Phi_B \) is the wavefunction of B and \( N \) is a normalization factor. Equation (5) is called a linear combination of atomic orbitals (LCAO). The probability density obtained by (5) will be:

\[ |\Psi_{\pm}|^2 = N^2(\Phi_A^2 + \Phi_B^2 \pm 2\Phi_A\Phi_B). \]  

(6)

What one should notice in equation (6) is the last term on the right hand side, \( \pm 2\Phi_A\Phi_B \). This term denotes either an enhancement in the probability density when the + sign is kept, or a reduction when the - sign is kept. To be more specific, the \( \Psi_+ \) molecular orbital gives a greater probability to find the electron in the internuclear region, due to the constructive interference of the atomic orbitals in this region. So the electron interacts with both nuclei and we have the formation of a bond. If \( \Psi_+ \) is occupied the formation of a bond is favored, so \( \Psi_+ \) is called a bonding orbital. In contrast, \( \Psi_- \) results from the destructive interference of atomic orbitals in the internuclear region, so if it is occupied the formation of a bond is not favored and \( \Psi_- \) is called an anti-bonding orbital.

Up to here we have seen the formation of \( \sigma \) and \( \pi \) bonds and the formation of molecular orbitals as a result of LCAO. Without explaining in detail, we mention that the main types of molecular orbitals are called \( \sigma \) and \( \pi \) orbitals and they can be bonding or anti-bonding. The electronic structure of homo-nuclear diatomic molecules can be determined easier due to their symmetry, whilst for polyatomic molecules certain methods and approximations have to be applied for the determination of their electronic structure.
2.2 Single and double photo-ionization

In general, by the term *ionization* we refer to the process where an atom or a molecule ejects a bound electron, after a sufficient amount of energy has been offered to the electron\(^2\). Thus, the kinetic energy of the electron is now greater than the electrostatic potential energy keeping it bound (binding energy) and the electron can be considered free. Due to the fact that the electrostatic interaction is weaker for valence electrons, the latter are the ones that can be observed easier in an ionization process because of their comparatively low binding energies.

If the energy to the electron is offered by a photon, the process is denoted as photo-ionization. Photo-ionization can be achieved using different light sources (He-lamp, LASER radiation, X-ray anodes) depending on whether we are interested in valence electrons or core electrons, for the latter high energy light sources are needed. The photo-ionization process involving a core electron is illustrated in figure 3. For the purposes of this thesis a He lamp was used which primarily allows for valence ionization and which we will describe in detail in the following section.

![Core electron photo-ionization](image)

The process illustrated in figure 3 can be characterized as Single Photo-ionization (SPI)\(^3\) due to the fact that only one electron is ejected after absorbing the energy offered by a single photon. It can be denoted as:

\[
\gamma + A \rightarrow A^+ + e^- \tag{7}
\]

where \(\gamma\) denotes the photon, \(A\) the neutral atom, \(A^+\) the singly ionized atom and \(e^-\) the ejected electron.

There are also cases where the absorption of a single photon leads to the ejection of two electrons. This process is referred to as Double Photo-ionization (DPI) and can be written as:

\[
\gamma + A \rightarrow A^{2+} + e^-_1 + e^-_2 \tag{8}
\]

The process described by equation 8 refers to direct DPI\(^3\). In contrast, in indirect DPI we have the ejection of a first electron transferring the singly-ionized atom into a metastable state \((A^+)^*\). This intermediate state may eventually eject a second electron in order to reach a more stable state. The whole process can be written as:

\[
\gamma + A \rightarrow (A^+)^* + e^-_1 \rightarrow A^{2+} + e^-_1 + e^-_2 \tag{9}
\]

As it can be understood, there will be a characteristic potential for each molecule in order for single photo-ionization to occur and a characteristic potential as well for double photo-ionization. According to energy conservation we get the following equations for single and double ionization respectively:

\[
E_1 = h\nu - \text{SIP} \quad E_1 + E_2 = h\nu - \text{DIP} \tag{10}
\]

where DIP is the double ionization potential, SIP is the single ionization potential and \(E_1, E_2\) the kinetic energies of the first and second emitted electrons respectively. The ratio between the lowest value of DIP
and lowest value of SIP was estimated by Tsai and Eland [4] to be:

\[
\frac{\text{DIP}}{\text{SIP}} = 2.7
\]  

(11)

Equation (11) can be applied to atoms. In the case of molecules most complicated effects such as dissociation, changes in geometry and mainly the distance of the two valence holes created should be taken under consideration.

Molloy et al. [5] suggested an empirical equation, where the the distance of the valence holes in the doubly ionized molecule can be determined if the lowest values of DIP and SIP are known:

\[
\text{DIP} = 2.20 \cdot \text{SIP} + \frac{11.5}{r_{h-h}},
\]  

(12)

where \(r_{h-h}\) is the distance of the valence holes in Ångström (Å).

Utilizing experimentally photo-ionization processes gives direct insights into the electronic structure of atoms and molecules. Since each electron in an atom or molecule has its characteristic binding energy, we can probe the electronic structure of an atom or a molecule by recording its photo-electron spectrum. Within the framework of the present thesis we recorded TOF photo-electron spectra of vinyl halides. The spectra obtained reflect the intensity distribution as a function of their TOF (i.e. the flight time it takes from the light-matter interaction point where they are created and until they reached the detector) or their electron kinetic/ binding energy. We will describe the experimental setup in detail in the following section. Moreover, in order to distinguish between the processes [8] and [9] we used a coincidence detection which will be described in what follows.

2.3 Auger transitions

The Auger effect is another phenomenon leading to the ejection of additional electrons from an atom. In figure 3 the emitted photo-electron creates a hole (the missing electron in the second picture) in the inner shell which is often referred to as a core hole. This core hole can now be filled by an electron from the valence shell and the energy liberated may cause the emission of a photon [3, 6] (radiative decay), or alternatively, a second electron may get ejected from the atom which is then referred to as an Auger electron. Figure 4 summarizes the whole process.

![Figure 4: The emission of an Auger electron upon the creation of a core hole and the emission of a photo-electron.](image)

3 Experimental setup

Figure 5 illustrates the experimental setup used in this thesis work. Briefly, radiation from a pulsed He lamp is used for ionizing the sample molecules. A strong permanent magnet combined with a weak solenoid field guides the electrons towards a micro-channel plate (MCP) detector where their arrival times are registered. In what follows we will describe in detail each of the components mentioned. The

\footnote{By the term hole we refer to the vacancy created in the spot previously occupied by the emitted electron.}
target gas is introduced into the spectrometer by a thin needle providing small sample doses. Vacuum pumps were used to keep various parts of the spectrometer including the flight tube vacuum at a pressure < 10^{-6} \text{ mbar}).

![Diagram of TOF spectrometer](image)

Figure 5: Schematic representation of the main parts of our TOF spectrometer illustrating its operation principle [3].

As soon as an electron is emitted it experiences the magnetic field created by the permanent magnet and the solenoid. The magnetic field guides all the electrons towards the detector independently of their initial velocities and without affecting their kinetic energies. Since the magnetic field plays a crucial role, we have to protect the electrons from auxiliary external magnetic fields acting as noise. For this purpose a \(\mu\)-metal shield mounted around the flight tube is used. Also, as it can be seen from figure 5 there is a second tube inside the flight tube which is electrically insulated from the other parts. This allows us to apply an electric field in order to ensure that even near zero kinetic energy electrons will reach the detector. The MCP detector consists of three plates and a fast timing read-out.

### 3.1 The He lamp

The He lamp used in our experiments was developed by John H.D. Eland at Oxford University[1],[7]. Photons are emitted by the lamp as a result of excitation of neutral or singly-ionized He atoms. The main idea for generating the photons is to utilize a discharge occurring in a hollow cathode which has been filled with He gas. The generation of the discharges can be understood by looking at figure 6 where the schematic circuit of the He lamp is shown.

![Diagram of He lamp](image)

Figure 6: The main parts of the He lamp [3].

A capacitor is connected to the hollow cathode and is charged up by a high voltage source about 10 kV. The other side of the capacitor is connected to a hydrogen thyratron which fires at high repetition rates, connecting this side of the capacitor, frequently to the earth. As a result there is an increase in
the cathode’s potential causing a discharge through the gas filled capillary. Since the atoms of the gas can be in various excited states, several transitions are possible which are listed in Table 2.

Table 2: List of transitions of He gas from an excited to a lower energy state.

<table>
<thead>
<tr>
<th>Atomic line</th>
<th>Electronic Transition</th>
<th>Wavelength (Å)</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He Iα</td>
<td>1s2s → 1s²</td>
<td>584.33</td>
<td>21.22</td>
</tr>
<tr>
<td>He I</td>
<td>2p² → 1s2p</td>
<td>320.29</td>
<td>38.71</td>
</tr>
<tr>
<td>He IIα</td>
<td>2p → 1s²</td>
<td>303.78</td>
<td>40.81</td>
</tr>
<tr>
<td>He IIβ</td>
<td>3p → 1s</td>
<td>256.32</td>
<td>48.37</td>
</tr>
<tr>
<td>He IIγ</td>
<td>4p → 1s</td>
<td>243.03</td>
<td>51.02</td>
</tr>
</tbody>
</table>

In order to select for the experiment a specific wavelength a toroidal grating monochromator was used. In our experiments the He Iα, He IIα and He IIβ lines were used.

3.2 The magnetic bottle spectrometer

In this subsection the magnetic bottle field effect is described in further detail. We will see how this effect makes it possible to record even those electrons which have been ejected in opposite direction in respect to the detector’s position, according to the original work of Kruit and Read [8], where it was originally described how the magnetic bottle field can be used in TOF experiments.

Let us consider the magnetic field shown in figure 7. As it can be seen the magnetic flux is very dense at one end and comparatively low further away, being reminiscent to a bottleneck. If we consider now an electron ejected at an angle $\theta_i$ with respect to the z-axis, having a velocity vector $\vec{v}$ and energy $E$, then the equation of motion for that electron will be:

$$\vec{F}_L = m\vec{\ddot{r}},$$

where $\vec{F}_L$ is the Lorentz force, which in this case is given by $\vec{F}_L = q(\vec{v} \times \vec{B})$. The velocity of the electron can be written as the sum of its parallel and transverse components, $v_\parallel$ and $v_\perp$, respectively and the cross product of the parallel component with the field will vanish. By solving equation 13 it can be seen that the electron will move on a helical trajectory with resonance frequency given by:

$$\omega = \frac{eB}{m_e}.$$  

The radius of the helix can be defined based on the fact that the Lorentz force is a centripetal force, so by equating the two forces we get:

$$r = \frac{m_e v_\perp}{eB} = \frac{v \sin \theta}{\omega}$$  

Figure 7: The magnetic bottle field. Two regions can be distinguished, one with high flux density and one with low flux density [8].
Now given an adiabatic variation of the field with respect to $z$, i.e., the interaction of the field on an electron changes negligibly during one revolution of the helical motion implies that the angular momentum of the motion with respect to the $z$-axis is a conserved quantity \[9\]. The norm of the angular momentum with respect to the $z$-axis will be according to equations 14 and 15:

\[
\ell = \frac{m_e v^2 \sin^2 \theta}{eB}.
\]  

So the angular momentum should be the same in the high density flux region and in the low density flux region. We get according to the notation used in figure 7 and equation 16:

\[
\frac{\sin \theta_f}{\sin \theta_i} = \sqrt{\frac{B_f}{B_i}}.
\]  

From equation 17 it can be seen that the initial angle $\theta_i$ which the velocity of the electron forms with the $z$-axis has been decreased to $\theta_f$, so the field drives all the electrons to the detector independently of their initial velocity. The principle described above is central to our experiments in order to detect electrons emitted in a different direction from the detector’s position including the detection of the low kinetic energy electrons.

### 3.3 MCP detectors

A detailed description of a MCP detector can be found in Ref. [10]. Briefly, a multichannel plate (MCP) is an array of $10^4$ to $10^7$ electron multipliers oriented parallel to each other can be used for the detection of electrons or ions, as well as for the detection of photons. Figure 8 taken from [http://adweb.desy.de/mdi/documentation/Restgas_at/PETRA/fmcp.gif](http://adweb.desy.de/mdi/documentation/Restgas_at/PETRA/fmcp.gif) and slightly modified shows this array.

![Figure 8: The parallel orientation of electron multipliers in a multichannel plate. The incident electron leads to the emission of multiple electrons due to a cascade effect.](http://adweb.desy.de/mdi/documentation/Restgas_at/PETRA/fmcp.gif)

An electron multiplier is essentially a coated glass tube structure (depicted in figure 8 as circle) that can multiply incident charges. The main process taking place in an electron multiplier is called secondary emission and which means the emission of secondary electrons when a single electron hits the emissary material with which these glass tubes are coated. Let us now suppose that $\delta$ secondary electrons are emitted by the incidence of a single electron. These $\delta$ secondary electrons will impinge again on the emissary material of the tube causing the emission of $\delta^2$ electrons and so on, so the gain of the multiplier will be $G = \delta^n$. By applying a potential difference at the edges of each multiplier we can collect all the secondary emitted electrons, so starting initially with a single electron we can get approximately a gain of $10^3$ electrons. This cascade process is schematically illustrated in figure 9 taken from [Ref. 10].
A single electron multiplier is called a channel and the main advantage of an MCP detector is that due to the many channels which it consists electrons emitted in various directions can efficiently be detected. What we did in the present experiments is to record the intensity of the emitted electrons as function of their TOF, thereby obtaining their TOF spectrum.

### 3.4 Time to energy conversion

From classical mechanics we know that:

\[
E_{\text{kin}} = \frac{m_e v^2}{2}
\]

\[
l = v \cdot t
\]

\[
\Rightarrow E_{\text{kin}} = \frac{m_e l^2}{2t^2}, \tag{18}
\]

where \(l\) is the length of the flight path and \(v\) the electron’s velocity. Because of a delay in the electronics used the detection of the electron, we have to subtract a constant time interval \(t_0\) from the measured time \(t\). In addition there will also be a contribution to the electron’s kinetic energy from the electrostatic field used to accelerate or decelerate electrons, which we can denote as \(E_0\). So equation (18) can be written as:

\[
E_{\text{kin}} = \frac{m_e l^2}{2(t - t_0)^2} + E_0 = \frac{D^2}{(t - t_0)^2} + E_0, \tag{19}
\]

where the constant \(D\) is \(D = \frac{m_e l^2}{2t_0^2}\) which is determined by a calibration process as well as the constants \(t_0\) and \(E_0\).

For the calibration procedure we record the photo-electron spectrum of a substance which is very well known. In our experiments we used the photo-electron spectrum of molecular oxygen \(O_2\), recorded at a photon energy of about 21 eV. The photo-electron spectrum of oxygen can be seen in figure [10]. In comparing to the spectra known in the literature [11], we can identify the binding energy corresponding to each peak (cf. Appendix [A]). Since we know the photon energy used, we can then calculate all the kinetic energies and the corresponding TOF. This is easily done by using a MatLab routine which solves a system of equations based on equation (19) resulting in the calibration parameters \(t_0, D, E_0\). Our calibration error was around 100-200meV.
Figure 10: The time of flight photoelectron spectrum of O$_2$ recorded with our TOF spectrometer at the photon energy of 21eV.

3.5 Coincidence maps

In order to understand coincidence maps, let us start from equations 8 and 9 discussed in subsection 2.2. Though both processes lead to the final emission of two electrons, in the first case they are emitted simultaneously and in the second case there is first a transition to singly charged intermediate state before the emission of the second electron occurs, as discussed in 2.2.

A direct way of disentangling the process described by 8 and the one described by 9 is to establish how the two electrons emitted are actually correlated. This can be achieved by plotting what is called a coincidence map which is essentially a diagram where one plots two different parameters measured simultaneously. Let us discuss how that works for 8 and 9.

In the plots displayed in figure 11, on the x-axis the energy of the first arrival electron emitted and on the y-axis the energy of the second arrival emitted electrons is shown, respectively.

Figure 11: Coincidence maps demonstrating direct DPI (left) and indirect DPI (right).

Electrons emitted in form of a direct DPI process will share the energy continuously giving a line (dashed) in such a coincidence map. In contrast the second plot illustrates indirect DPI where both electrons detected correspond to single discrete values. Thus, in the latter case, we get a point in the coincidence map, shown in figure 11 as a colored dot.

4 Results and discussion

In this section we will present the results obtained for C$_2$H$_3$Br, C$_2$H$_3$Cl and C$_2$H$_4$ molecules. The geometric structure of those molecules are shown in figures 12a, 12b, and 12c. For those figures, the software
Jmol was used which is an open-source Java viewer for chemical structures in 3-D and can be found at http://www.jmol.org/

(a) The vinyl bromide molecule.  (b) The vinyl chloride molecule.  (c) The ethylene molecule.

Figure 12: The structures of vinyl bromide, vinyl chloride and the corresponding non-halide compound, the ethylene molecule.

From our TOF electron (coincidence) data measured for the above molecules the SIP and DIP can be extracted, by using equation 19. This will give us the kinetic energy of the emitted electrons, e.g. in the case of the 21 eV recordings, by subtracting the kinetic energies from the photon energy we can get the binding energy (SIP) of the singly ionized valence electronic states of the molecules. The calibration parameters in equation 19 have been determined based on the molecular oxygen spectrum as explained before. In order to obtain electron data associated with double ionization (DIP), we have to increase the photon-energy in order for DPI to occur. The TOF of both electrons will then be recorded pairwise, and equation 19 can be applied for both electrons. Finally from the second of equations 10 the DIP can be established. The SIP plot for photon energy of 21eV can be seen in figure 13. In order to get the DIP for the molecules studied we plotted a coincidence map for each molecule showing the TOF of the first vs the second electron, as well as the kinetic energy of the first vs the second electron. From these plots we have the data required to proceed as described above and get the DIP for each molecule.

Figure 13: Single ionization electron spectra recorded at the photon energy of He Iα for $C_2H_3Br$, $C_2H_3Cl$, $C_2H_4$. 
At that point we have to present the coincidence maps for $\text{C}_2\text{H}_3\text{Br}$ and $\text{C}_2\text{H}_3\text{Cl}$. First we show the TOF-TOF coincidence maps for 41eV and 48eV photon energy and then the coincidence maps showing the kinetic energy of the first electron vs the kinetic energy of the second electron.

![TOF coincidence maps for $\text{C}_2\text{H}_3\text{Br}$ and $\text{C}_2\text{H}_3\text{Cl}$ for 41eV photon energy.](image1)

(a) Coincidence map showing the TOF of the first vs the second electron for $\text{C}_2\text{H}_3\text{Br}$, for 41eV photon energy.

(b) Coincidence map showing the TOF of the first vs the second electron for $\text{C}_2\text{H}_3\text{Cl}$, for 41eV photon energy.

Figure 14: Coincidence maps showing the TOF of the first vs the second electron for $\text{C}_2\text{H}_3\text{Br}$ and $\text{C}_2\text{H}_3\text{Cl}$ for 41eV photon energy.

From figures 14a and 14b, we see that as the TOF of the first electron decreases (fast electron), the TOF of the second increases and vice versa (a curve starting from (1500,1500) and ends at (6000,1000) as inverse square demonstrates that fact). We expect this inverse square form of the line, from the fact that we have squared time in equation 19. Now if we plot the coincidence map showing the kinetic energy of the first vs the kinetic energy of the second electron we expect to see some straight lines showing an energy sharing as in figure 11. In this case we have a straight line again because of the form of equation 19. The coincidence maps for the kinetic energy of the first vs the second electron, for the same molecules at 41eV again are shown in figure 15.

The straight lines indicating direct DPI can be seen in figures 15a and 15b starting from (0,12) and ending at (7,7). So we can say that primarily we have direct DPI. In order to validate our experimental results, we plot the same coincidence maps for the same molecules, but this time for 48eV photon energy. In figure 16 we can see the TOF coincidence maps and in figure 17 the kinetic energy coincidence map. Also for this photon energy we can say that primarily we observe direct DPI.

In figures 18 and 19 we have the coincidence maps showing the DIP vs the kinetic energy of the first electron for $\text{C}_2\text{H}_3\text{Br}$ and $\text{C}_2\text{H}_3\text{Cl}$ at 41eV and 48eV respectively. Then in figures 20 and 21 we have plotted the intensity vs DIP for both photon energies, as we did for SIP in figure 13.

The conclusions from the 41eV plots can also be obtained from the 48eV plots as similar lines can be observed in the coincidence maps. The straight lines in the coincidence map showing the kinetic energy of the first vs the second electron (cf. figures 17a and 17b) start at (0,20) and end at (10,10). The TOF coincidence maps in figures 16a and 16b have also the same line demonstrating primarily direct DPI as
Figure 15: Coincidence maps showing the kinetic energy of the first vs the second electron for $C_2H_3Br$ and $C_2H_3Cl$ for 41eV photon energy.

in the 41eV photon energy case.
(a) Coincidence map showing the TOF of the first vs the second electron for \( C_2H_3Br \), for 48eV photon energy.

(b) Coincidence map showing the TOF of the first vs the second electron for \( C_2H_3Cl \), for 48eV photon energy.

Figure 16: Coincidence maps showing the TOF of the first vs the second electron for \( C_2H_3Br \) and \( C_2H_3Cl \) for 48eV photon energy.

(a) Coincidence map showing the DIP vs the kinetic energy of the first electron for \( C_2H_3Br \) at 41eV.

(b) Coincidence map showing the DIP vs the kinetic energy of the first electron for \( C_2H_3Cl \) at 41eV.

Figure 18: Coincidence maps showing the DIP vs the kinetic energy of the first electron for \( C_2H_3Br \) and \( C_2H_3Cl \) at 41 eV.
(a) Coincidence map showing the kinetic energy of the first vs the second electron for
$C_2H_3Br$, for 48eV photon energy.

(b) Coincidence map showing the kinetic energy of the first vs the second electron for
$C_2H_3Cl$, for 48eV photon energy.

Figure 17: Coincidence maps showing the kinetic energy of the first vs the second electron for $C_2H_3Br$
and $C_2H_3Cl$ for 48eV photon energy.

From figure 13 the lowest SIP for $C_2H_3Br$, $C_2H_3Cl$ and $C_2H_4$ can be extracted. One can assign this
value to each molecule either by considering the onset of the very first peak in plot 13 or by considering
the value corresponding to the maximum of the very first peak (called as onset and vertical values
respectively). The first is what we did in the framework of this thesis. From plots 18 and 19 one can get
the value of DIP for each molecule.
(a) Coincidence map showing the DIP vs the kinetic energy of the first electron for $C_2H_3Br$ at 48eV.

(b) Coincidence map showing the DIP vs the kinetic energy of the first electron for $C_2H_3Cl$ at 48eV.

Figure 19: Coincidence maps showing the DIP vs the kinetic energy of the first electron for $C_2H_3Br$ and $C_2H_3Cl$ at 48 eV.

Figure 21: Double ionization electron spectra for $C_2H_3Br$, $C_2H_3Cl$ and $C_2H_4$, recorded at the photon energy of He II$\beta$. 18
As it can be seen from plots 20 and 21, the DIP doesn’t change when we go to higher photon energies as it was expected. At that point we should remember that the emitted electrons upon the absorption of a 48eV photon will have higher kinetic energy (cf. equations 10). Since the flight tube of our spectrometer was relatively short (2.2m) resolution for high kinetic energy electrons is not as good as compared to the lower kinetic energies obtained when using 41eV photon energy. That is the reason why figure 20 is better resolved than figure 21. Still one can see the same peaks for each molecule and can extract the same values for the lowest DIP.

At that point we have to say that the TOF photo-electron spectra which are the base of all the previous plots can be seen in the appendices B and C. In addition the DIP for \( \text{C}_2\text{H}_4 \) has been measured as for \( \text{C}_2\text{H}_3\text{Br} \) and \( \text{C}_2\text{H}_3\text{Cl} \), but we have not presented the relative coincidence maps.

From our experimental values now, we can estimate the ratio DIP/SIP, as well as the distance \( r_{h-h} \) of the valence holes created, from equation 12. All the data and the calculated holes-distance are summarized in Table 3.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>SIP (eV)</th>
<th>DIP (eV)</th>
<th>DIP/SIP</th>
<th>( r_{h-h} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_3\text{Br} )</td>
<td>9.36</td>
<td>27.04</td>
<td>2.89</td>
<td>1.78</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_3\text{Cl} )</td>
<td>9.57</td>
<td>27.89</td>
<td>2.91</td>
<td>1.68</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>10.03</td>
<td>30.32</td>
<td>3.02</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Table 3: The calculated distances of the holes in the dication according to equation 12 using the SIP and DIP values measured in this thesis.

The interpretation of the results presented in Table 3 is not trivial. In order to decide whether the distances estimated by equation 12 are valid, \textit{ab initio} theoretical calculations are needed according to the work of Linusson et al. 12, in order to argue about the nature of the outermost valence orbital, something that was not possible within the time limits of the present thesis. According to Kimura et al. 13 the outermost valence orbital in \( \text{C}_2\text{H}_3\text{Br} \), \( \text{C}_2\text{H}_3\text{Cl} \) and \( \text{C}_2\text{H}_4 \) is of \( \pi \) C-C character. That means that the specific orbital is a bonding orbital contributing to the bonding between the carbon atoms. The ejection of two electrons by the outermost valence orbital should result an increase in the bond length between the carbon atoms. That can become obvious either by considering that the two electrons were ejected by a bonding orbital or by considering the Coulomb repulsion between the two valence holes.
created in that orbital. In Table 4 there is a comparison between the distance of the carbon atoms in
the neutral molecule and the one estimated by equation 12.

<table>
<thead>
<tr>
<th></th>
<th>C-C</th>
<th>C-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_2H_3Br)</td>
<td>1.33</td>
<td>1.78</td>
</tr>
<tr>
<td>(C_2H_3Cl)</td>
<td>1.31</td>
<td>1.68</td>
</tr>
<tr>
<td>(C_2H_4)</td>
<td>1.32</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Table 4: Comparison between the distances of the carbon atoms in the neutral molecule and the distance
of the holes by equation 12

As it can be seen, in all three cases there is an increase in the bond length between the carbon
atoms, thus the holes distance that equation 12 estimates is in agreement with some rough theoretical
predictions. Finally, summarizing the results of this thesis we can say that the double ionization processes
taking place in the molecules studied are primarily direct but still we can not exclude indirect processes
taking place. If we could have better resolution in the kinetic energy of the second ejected electron then
it still probable to see a constant amount of kinetic energy for the second electron which might be due
to auto-ionization or Auger transitions, so in this case indirect ionization can be observed. Moreover,
the values of the holes distance calculated by equation 12 are in agreement with theoretical predictions,
but in order for that equation to be used \textit{ab initio} calculations should have taken place first, so that the
nature of the outermost valence orbital is known.

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References

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[3] Per Linusson, \textit{Single-photon multiple ionization processes studied by electron coincidence spec-
troscopy}, Ph.D thesis, Stockholm University

143-165, 1980


University


A The O₂ photo-electron spectrum

The TOF photo-electron spectrum as it was recorded by our TOF spectrometer in Uppsala University is the one shown in figure [10] and presented again in this appendix.

The binding energy of each peak is known [11] and in Table 5 the states and the binding energies of the peaks observed are presented.

<table>
<thead>
<tr>
<th>State</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X²Π&lt;sub&gt;g&lt;/sub&gt;</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>12.3</td>
</tr>
<tr>
<td>α¹Π&lt;sub&gt;u&lt;/sub&gt;</td>
<td>16.7</td>
</tr>
<tr>
<td>b¹Σ&lt;sup&gt;-&lt;/sup&gt;&lt;sub&gt;g&lt;/sub&gt;</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>18.6</td>
</tr>
<tr>
<td></td>
<td>18.7</td>
</tr>
<tr>
<td>B²Σ&lt;sup&gt;-&lt;/sup&gt;&lt;sub&gt;g&lt;/sub&gt;</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td>20.8</td>
</tr>
</tbody>
</table>

Table 5: Electronic states and binding energies of the peaks recorded at O₂ photo-electron spectrum by our TOF spectrometer at Uppsala University.

The two first peaks representing the X²Π<sub>g</sub> states as well as the five peaks representing the b¹Σ<sup>-</sup><sub>g</sub> states are not clearly depicted. Also the second peak, representing the α¹Π<sub>u</sub> states is consisting of several peaks according to [11], but due to resolution errors we consider only one peak and assign the binding energy corresponding to the most intense of the peaks. Finally, five peaks representing the B²Σ<sup>-</sup><sub>g</sub> states were observed. We mention here one more time that our calibration errors were ≈ 100-200meV.
B The 41eV photon energy spectra
C The 48eV photon energy spectra