

UNIVERSITY OF CRETE DEPARTMENT OF PHYSICS

MASTER'S THESIS

# Photodissociation of CH<sub>2</sub>Br<sub>2</sub> and CHBr<sub>3</sub> at 193 nm

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## Abstract

The photodissociation of halogen-containing molecules, especially those containing Cl and Br, has received the attention of scientists due to the role these species play in stratospheric ozone depletion. Bromine is said to be 40 times more effective than chlorine on the destruction of ozone. In this master's thesis, I present results on the photodissociation dynamics of CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> at 193 nm using the Velocity Map Imaging technique. We recorded images of C<sup>+</sup>, CH<sup>+</sup>, CH<sup>+</sup><sub>2</sub>, Br<sup>+</sup>, CH<sub>2</sub>Br<sup>+</sup> and CH<sub>2</sub>Br<sup>+</sup><sub>2</sub> for dibromomethane and H<sup>+</sup>, C<sup>+</sup>, CH<sup>+</sup>, Br<sup>+</sup>, CBr<sup>+</sup>, CHBr<sup>+</sup><sub>2</sub> and CHBr<sup>+</sup><sub>3</sub> for bromoform. By analyzing the kinetic energy release of the photofragments, we were able to identify the most probable dissociation channels for both molecules.

The first chapter introduces the molecular dynamics field, as well as fundamental theory for the photodissociation of molecules and the Velocity Map Imaging technique. The second chapter contains the experimental setup that we utilized. In the third and fourth chapters, I present the results of the photodissociation of dibromomethane and bromoform with an ArF excimer laser, i.e. the KER distributions of the ions and the most probable processes and channels.

# Περίληψη

Η φωτοδιάσπαση των μορίων που περιέχουν αλογόνα, ειδικά εκείνων που περιέχουν χλώριο και βρώμιο, έχουν ελκύσει το ενδιαφέρον των επιστημόνων λόγω του ρόλου που παίζουν στην μείωση του όζοντος που βρίσκεται στη στρατόσφαιρα. Έχει υποθεί ότι το βρώμιο είναι 40 φορές πιο αποτελεσματικό από το χλώριο στην καταστροφή του όζοντος. Σε αυτή τη μεταπτυχιακή εργασία θα παρουσιάσω αποτελέσματα της δυναμικής της φωτοδιάσπασης του βρωμοφορμίου και του διβρωμομεθανίου στα 193 nm χρησιμοποιώντας την τεχνική απεικόνισης χαρτογράφησης ταχυτήτων. Καταγράψαμε εικόνες των C<sup>+</sup>, CH<sup>+</sup>, CH<sup>+</sup><sub>2</sub>, Br<sup>+</sup>, CH<sub>2</sub>Br<sup>+</sup> και CH<sub>2</sub>Br<sup>+</sup><sub>2</sub> για το διβρωμομεθάνιο και H<sup>+</sup>, C<sup>+</sup>, CH<sup>+</sup>, Br<sup>+</sup>, CBr<sup>+</sup>, CHBr<sup>+</sup><sub>2</sub> και CHBr<sup>+</sup><sub>3</sub> για το βρωμοφόρμιο. Αναλύοντας την κινητική ενέργεια των φωτοθραυσμάτων, μπορούσαμε να ταυτοποιήσουμε τα πιο πιθανά κανάλια διάσπασης για τα δύο αυτά μόρια.

Το πρώτο κεφάλαιο εισάγει το πεδίο της μοριαχής δυναμικής, όπως επίσης και θεμελιώδη θεωρία για την φωτοδιάσπαση των μοριών και την τεχνική απεικόνισης χαρτογράφησης ταχυτήτων. Το δεύτερο κεφάλαιο περιέχει την πειραματική διάταξη που χρησιμοποιήσαμε. Στο τρίτο και στο τέταρτο κεφάλαιο παρουσιάζονται τα αποτελέσματα από τη φωτοδιάσπαση του διβρωμομεθανίου και του βρωμοφορμίου με ένα ArF excimer laser, δηλαδή της κατανομές της κινητικής ενέργειας των ιόντων και των πιο πιθανών διεργασιών και καναλιών.

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## Chapter 1

## Introduction

### **1.1 Molecular Dynamics**

The molecular dynamics field studies the forces that arise during physical or chemical events, such as photoionization

$$AB + hv \longrightarrow AB^+ + e^- \tag{1.1}$$

where an electron is emitted after the atom absorbs one or more photon(s), photodissociation

$$AB + hv \longrightarrow A + B \tag{1.2}$$

where the bond between the atoms breaks, or a chemical reaction

$$AB + C \longrightarrow A + BC \tag{1.3}$$

A lot of problems in this field require the simultaneous measurement of a particle's speed and angular direction. Many studies in the field, such as photodissociation of a molecule, can be understood only if the internal energies and velocities of all products are determined. In this thesis, we are interested in photodissociation, i.e. the one reactant is electromagnetic radiation (light) and the other is the molecule to be studied.

#### 1.1.1 Potential Energy Surfaces

A potential energy surface (PES) shows the potential energy of a molecule as a function of geometry. PESs represent potential energy of a chemical system as a function of the relative internuclear positions of the atoms or molecules that participate in a reaction. We can construct a PES, given that we have experimental data and quantum chemical analysis.

PES are useful because they allow us to plot the energy variations as a reaction takes place, as well as how possible a certain reaction is to occur. In order to fully comprehend the mechanism behind a given reaction, we need PES.

The PES of water is represented in Figure 1.1. It is obvious that there are two degrees of freedom, since the molecule has two bonds.

PES can be classified as attractive or repulsive. In the first case, the products are formed as the distance between the reactants decreases, whereas in the latter, the products are formed as the distance between the reactants increases.



Figure 1.1: PES of H<sub>2</sub>O, Wikipedia

## **1.2 Photofragment Imaging**

### **1.2.1** Conservation of Momentum

Suppose that we have the molecule AB that dissociates when photolyzed by a laser, producing the reaction

$$AB + hhv \longrightarrow A + B \tag{1.4}$$

We assume that AB has no initial energy and is in its ground vibrational state (v=0). The total energy is

$$E = T_A + T_B \tag{1.5}$$

The photon energy would be spent in dissociating the A-B bond (D<sub>0</sub>) and in kinetic (T<sub>A</sub>, T<sub>B</sub>) and internal (E<sub>I</sub>(A), E<sub>I</sub>(B)) energy of the photofragments.

$$E_{av.} = hv - D_0 - E_I(A) - E_I(B)$$
(1.6)

Due to conservation of momentum, we have

$$\vec{p}_i = \vec{p}_f = 0 \longrightarrow m_A \vec{v}_A = m_B \vec{v}_B \tag{1.7}$$

Combining equations 1.5 and 1.7, we get the energies for the two fragment

$$T_B = \frac{m_A}{m_{tot.}} E_{av.} \quad , \quad T_A = \frac{m_B}{m_{tot.}} E_{av.} \tag{1.8}$$

where  $m_{tot.} = m_A + m_B$  and  $E_{av.}$  is the total excess kinetic energy left over after deducting the internal energies of A and B. In this regard, measuring the kinetic energy release of one of the two fragments translates into knowledge of the kinetic energy release of the other. It is obvious that if photoionization takes place, then the electron takes all of the  $E_{av.}$ , being the much lighter mass than the ionized radical, whereas if a homonuclear diatomic molecule dissociates, then the total kinetic energy release is distributed equally between the two atoms since they have the same mass.

## **1.2.2** Molecular Internal Energy

#### **Spin-Orbit Coupling**

The spin of an electron produces a magnetic moment. Similarly, the orbital angular momentum  $(\ell)$  produces a magnetic moment if the electron is in an orbital  $\ell > 0$ . Spin orbit coupling is the interaction of the spin magnetic moment  $\vec{\mu}$  with the magnetic field  $\vec{B}$  that arises from the orbital angular momentum  $\ell$ .

The quantity that can describe the interaction is the total angular momentum  $\vec{j}$ , where  $\vec{j} = \vec{l} + \vec{s}$ . The energies of the levels are given by<sup>1</sup>

$$E_{\ell,s,j} = \frac{1}{2}hcA[j(j+1) - \ell(\ell+1) - s(s+1)]$$
(1.9)

where A is the spin-orbit coupling constant expressed in wavenumbers  $(cm^{-1})$ .

#### Term Symbols in Atoms

The conventional atomic term symbol has the form

$$^{2s+1}L_j \tag{1.10}$$

where  $\vec{\mathbf{L}}$  is the total orbital angular momentum number  $(\vec{L} = \vec{\ell_1} + \vec{\ell_2})$ , **j** is the total angular momentum number  $(\vec{j} = \vec{j_1} + \vec{j_2})^{-1}$  and (2s+1) is the spin multiplicity. The designation of orbitals is S if L=0, P if L=1, D if L=2, F if L=3, etc.

#### **Electronic Selection Rules**

The key parameter that determines if a transition can take place is  $\mu_{if}$ , which is the transition dipole moment

$$\vec{\mu}_{if} = \langle \psi_i^* \mid \vec{\mu} \mid \psi_f \rangle = \int \psi_i \vec{\mu} \, \psi_f d\tau = q \int \psi_i \vec{r} \, \psi_f d\tau \qquad (1.11)$$

The physical meaning of  $\vec{\mu}$  is that of the charge redistribution after a transition<sup>1</sup>. A transition is "allowed" if the integral of eq. 1.11 is non-zero, and "forbidden" if it is equal to zero. Symmetry plays significant role in which transitions can happen. In atomic spectra, the selection rules are the following

$$\Delta S = 0, \ \Delta L = 0, \pm 1, \ \Delta \ell = \pm 1, \ \Delta J = 0, \pm 1$$
(1.12)

#### Molecular Term Symbols

The general form of a molecular term symbol is

$$^{2S+1}\Lambda^{(+,-)}_{\Omega,\ (g/u)}$$
 (1.13)

where S is the total spin of the system,  $\Lambda$  is the orbital angular momentum's projection and  $\Omega$  is the total angular momentum, both along the internuclear axis.  $\Lambda$  can take values 0, 1, 2, 3,... which in spectral terms are denoted as  $\Sigma$ ,  $\Pi$ ,  $\Delta$ ,  $\Phi$ ,... The symmetry or parity of the system is indicated by the subscript g/u, where g stands for gerade (even in german) and u stands for ungerade (odd). This subscript is used to label the electronic states of diatomic molecules. Furthermore, the (+,-) superscript is the reflection symmetry along an arbitrary plane containing the internuclear axis.

 $\vec{k} = \vec{k_1} + \vec{k_2}, \vec{k_1} + \vec{k_2} - 1, \dots, |\vec{k_1} - \vec{k_2}|$ 

#### **Molecular Selection Rules**

Just like in atoms, molecules obey selection rules. These are

$$\Delta J = 0, \pm 1 \text{ (forbidden for } J = 0 \leftrightarrow J = 0\text{)}, \ \Delta S = 0, \ u \leftrightarrow g, \ + \leftrightarrow - \tag{1.14}$$

Besides the selection rules presented above, there are also Hund's coupling cases

$$\Delta \Lambda = 0, \pm 1, \ \Delta \Omega = 0, \pm 1 \ (\Delta J = 0 \text{ forbidden for } \Omega = 0 \leftrightarrow \Omega = 0), \ \Delta \Sigma = 0$$
(1.15)

The charge redistribution must be polar in order to have a possible transition.

#### **Rotational Internal Energy**

The main parameter is the moment of inertia I, which for a diatomic molecule is

$$I = \mu r_i^2 \tag{1.16}$$

where

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \tag{1.17}$$

with  $m_i$  being the mass of each atom and  $r_i$  is the distance perpendicular to the atom *i* of the rotation axis. If a molecule can rotate about two axis, then the energy of the molecule is

$$E = \frac{1}{2}I_a\omega_a^2 + \frac{1}{2}I_b\omega_b^2$$
(1.18)

Since  $J = I\omega$ , then

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b}$$
(1.19)

Let's assume the case of the spherical rotor, where  $I_a = I_b$  and  $J^2 = J_a^2 + J_b^2$ . In quantum mechanics, the Hamiltonian that describes the system is

$$\hat{H} = \frac{J^2}{2I} \tag{1.20}$$

and when acted on a wavefunction  $|\psi\rangle$ , we get

$$\hat{H}|\psi\rangle = \hbar^2 j(j+1)|\psi\rangle \tag{1.21}$$

As a result, we get

$$E_{rot.} = hcBJ(J+1) \tag{1.22}$$

in which  $B = \frac{\hbar}{4\pi cI}$  being the rotational constant. The transition moment vanishes unless the following conditions are fulfilled:

$$\Delta J = \pm 1, \ \Delta M_J = 0, \ \pm 1 \tag{1.23}$$

#### **Vibrational Internal Energy**

The molecular potential energy curve can be expanded around its minimum by using a Mclaurin series

$$V(x) = V(0) + (\frac{\partial V}{\partial x})_0 x + \frac{1}{2} (\frac{\partial^2 V}{\partial x^2})_0 x^2 + \dots$$
(1.24)

Since the series is around the minimum, the second term is 0. The first term is a constant, so we can assume that it is equal to zero. Thus, the only term that is not zero in this approximation is the third one, where we can define the force constant as

$$k = \left(\frac{\partial V}{\partial x}\right)_0 \tag{1.25}$$

Adding this potential into the Schrödinger equation, we can derive the permitted vibrational energy levels

$$E_{vib.} = (v + \frac{1}{2})\hbar\omega \tag{1.26}$$

where v=0, 1, 2,... and  $\omega = \sqrt{\frac{k}{\mu}}$ , ( $\mu$  is the reduced mass of the molecule).

An approximation that works better than the method discussed above is the anharmonic oscillator model, which is given by the formular

$$E_{vib.} = \hbar \omega [(v + \frac{1}{2}) - (v + \frac{1}{2})^2 \omega_e \chi_e + (v + \frac{1}{2})^3 \omega_e y_e - \dots]$$
(1.27)

where  $\omega_e \chi_e$  is the second term of the anharmonicity vibrational constants and  $\omega_e y_e$  the third one.

#### 1.2.3 Photodissociation

Photodissociation is the mechanism in which, after photolysis, the bond of the molecule breaks. It is described by Equation 1.2. Suppose that we have the dissociation process shown in Equation 1.4. Due to conservation of energy, we have

$$E(AB) + nhv = D_0 + E_I(A) + E_I(B) + T(A) + T(B)$$
(1.28)

where

- E(AB) is the internal energy of the AB molecule
- *nhv* is the energy of the photons
- $D_0$  is the bond dissociation energy
- $E_I(A)$  and  $E_I(B)$  are the internal energies of A and B, respectively
- T(A) and T(B) are the kinetic energies of A and B, respectively

The bond dissociation energy is the energy required to break a certain bond in polyatomic molecules. The bond dissociation energy in diatomic molecules is given by the following equation<sup>2</sup>

$$D^{o}_{298}(AB) \approx D^{o}(A-B) + \frac{3}{2}RT = D^{o}(A-B) + 3.7181 \text{ kJ/mol}$$
 (1.29)

whereas for polyatomic molecules the formula below is utilized

$$D^{o}_{298} = \Delta_f H^{o}(R) + \Delta_f H^{o}(X) - \Delta_f H^{o}(RX)$$
(1.30)

where  $\Delta_f H^{o}(i)$  is the enthalpy of the atoms or radicals.



Internuclear Distance

Figure 1.2: Photodissociation process of the AB molecule

The internal energy that a fragment can acquire varies. It can be electronic, vibrational or rotational energy if the fragment is a molecular radical, or electronic if the fragment is an atom. Heat transfer to or from the surrounding, changes in temperature and pressure and interaction with radiation can influence the internal energy of a fragment. More information on the internal energy of the photofragments will be given in the next chapter.

The internal energy of AB, E(AB), can be considered to be zero without significant impact on our calculations since we have a molecular beam that is ~ 5-30K. This means that the molecule AB is in its ground state with no vibrations.

In Figure 1.2, the process of photodissociation is shown. The blue graph is that of molecule AB and the green one is that of the excited states of said molecule. It is obvious that as the internuclear distance increases, there is no longer a potential well but something like a straight line, which indicates the dissociation of the molecule. Similar things can be said for the green graph, where in a large internuclear distance we get  $A + B^*$ . These occur because as the energy and the distance between the two nuclei increases, it is easier for a bondage break between A and B to happen.

These two graphs demonstrate attractive PES. They are characterized by their lower potential energy correspondence and their minima (stable states). Also, bound electronic, vibrational or rotational states of a molecule are attractive.

The red graph represents a repulsive state. These states are generally unstable and have small lifetimes. As a result, they do not have any minima or stable points.

### **1.2.4** Angular Distribution of Photofragments

Since the inception of molecular dynamics field, angular distribution has played a pivotal role in understanding the processes that underlie experiments of a molecular beam with another beam, e.g. laser radiation. In 1963, Zare and Herschbach<sup>3</sup> published their work in which they studied the correlation of a fragment's velocity  $\vec{v}$  and its parent's transition dipole moment  $\vec{\mu}$ . If the light beam ( $\vec{\epsilon}$ ) propagates in a direction that is either parallel

or perpendicular to the velocity of the molecule, then the angular distribution of the fragments will exhibit peaks. This occurs because the absorption probability is proportional to  $\vec{\mu}_{if}$  and  $\vec{\epsilon}$ , that is

$$\mathbf{P}_{\text{abs.}} \propto \mid \boldsymbol{\mu}_{if} \cdot \vec{\boldsymbol{\varepsilon}} \mid^2 \tag{1.31}$$

where  $\mu_{if}$  is the transition dipole moment. The form of the anisotropy is described by eq. 1.31. In 1972, Zare expanded this work further<sup>4</sup>, providing the formula for the angular distribution

$$I(\theta) = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)]$$
(1.32)

where

$$P_2(\cos\theta) = \frac{3\cos^2\theta - 1}{2} \tag{1.33}$$

is the second order Legendre polynomial,  $\beta$  is the asymmetry parameter and the  $1/4\pi$  term is the normalization factor. The  $\beta$  parameter is an extremely important quantity, as it can predict the type of transition in a molecule, following the absorption of photons from the incident light beam. The values of this parameter range,  $-1 \le \beta \le 2$ . From this range of values, three of them show exactly what type of transition is occurring, the light beam is polarized:

• If  $\beta=2$ , then the transition is parallel  $(I(\theta) \propto \cos^2 \theta)$ , i.e. the transition dipole moment  $\mu$  is aligned to the velocity  $\vec{v}$  of the products.



Figure 1.3: Parallel transition

• If  $\beta$ =-1, then the transition is perpendicular ( $I(\theta) \propto \sin^2 \theta$ ), i.e.  $\vec{\mu} \cdot \vec{v}=0$ .



Figure 1.4: Penpendicular transition

• If  $\beta=0$ , then there is no anisotropy, as  $I(\theta)$  remains constant, and there is an isotropic angular distribution.

Examples of parallel transitions are  $\Sigma \to \Sigma$  and  $\Pi \to \Pi$ , whereas perpendicular ones are transitions such as  $\Sigma \to \Pi$  and  $\Pi \to \Delta$ .

In the case of multiphoton transitions, eq. 1.32 becomes more complex, i.e.

$$I(\theta) \propto \sum_{n} a_{2n} P_{2n}(\cos \theta) \tag{1.34}$$

where for a 2-photon process,  $a_2 = \beta$  and  $a_4 = \gamma^5$ . Furthermore, if the molecule is not diatomic but polyatomic, then the limit of rapid dissociation ( $\beta$ =-1 and  $\beta$ =2) becomes

$$\beta = 2P_2(\cos a) \tag{1.35}$$

in which *a* is angle between the bond of the molecule and the transition dipole moment  $\vec{\mu}_{if}$ .

## **1.3 Multi-Photon Ionization**

Multi-Photon Ionization (MPI) is the phenomenon in which an atom or molecule absorbs multiple photon simultaneously, followed by electron ejection and as a result, ionization. Some atoms or molecules may require one photon in order to exceed the ionization potential threshold, hence named Single-Photon Ionization (SPI), as shown in Figure 1.5 by the red arrow, others may require two, three or more photons in order to cross the ionization barrier, hence the name MPI. This is possible due to the advances of laser technology, since with a higher laser intensity, there are more photons per square area. In MPI, the atom or molecule transitions from the ground state to an intermediate and/ or virtual state before being ionized.

Virtual states are "imaginary states" since they do not represent an eigenfunction of any operator. These states are short-lived  $(10^{-18} - 10^{-15} \text{ s})$  since they violate the relation between energy and momentum that is otherwise respected in stationary states.

Besides SPI and MPI, there is also a special case of Multiphoton Ionization and is called REMPI, which stands for Resonance-Enhanced Multiphoton Ionization. REMPI usually is divided in two parts. In the first part, the molecule absorbs n photons of a certain wavelength in order to reach an electronically excited intermediate state and then m' photons ionize the molecule.

In general, photoionization through MPI and REMPI can be described as

$$AB + nhv \longrightarrow AB^* \longrightarrow AB^+ + e^- \tag{1.36}$$



Figure 1.5: Single-Photon Ionization, Multi-Photon Ionization and REMPI

## **1.4 Molecular beams**

The nozzle, or free-jet, molecular beam is a neutral beam is produced through an underexpanded, supersonic, continuum jet expansion by extracting it from a high-pressure gas source into a low-pressure ambient background. A 2D representation can be shown in Figure 1.6.

The gas flows from a insignificantly small velocity named the stagnation state, with pressure  $P_0$  and temperature  $T_0$ , that is the nozzle, to the source exit, which is the chamber. This is possible due to the difference in pressure ( $P_0 - P_b$ ) and the decreased area, which allow the acceleration.

There are three important parameters that describe the flow:

- The Mach number, M, which is the ratio of the velocity of a fluid to the velocity of sound in that fluid.
- The ratio of the stagnation state pressure  $P_0$  to that of the background pressure  $P_b$ ,  $\frac{P_0}{P_b}$ , and
- The critical value  $G \equiv (\frac{\gamma+1}{2})^{\frac{\gamma}{\gamma-1}}$ , which is smaller than 2.1 for all gases.

 $\gamma$  is the ratio of the system's heat capacities, namely

$$\gamma = \frac{C_p}{C_v} \tag{1.37}$$



Figure 1.6: Continuum free-jet expansion, based on the schematic of Scoles<sup>6</sup>

The speed of the gas flow is characterized by three cases:

- Subsonic, where the speed of the gas flow is smaller than that of the local speed of sound, i.e. M<1 and  $\frac{P_0}{P_b}$ <G. The exit pressure is approximately equal to  $P_b$  without any additional expansion.
- Sonic, where the two velocities are equal in magnitude, i.e.  $M=1 \frac{P_0}{P_b} > G$ . The exit pressure is independent of the background pressure and the flow is called "underexpanded" since the pressure at the exit is larger than the ambient one. A subsequent expansion happens as the flow tries to meet the required boundary conditions mandated by  $P_b$ .
- Supersonic, where the speed of the gas flow is larger than the local speed of sound, i.e. M>1. In this state of flow, the velocity increases as the flow area becomes bigger. Furthermore, since the fluid propagates faster than the information which moves at the speed of sound, supersonic flow does not need to oblige to the boundary conditions, although it must adjust.

The solution to the last bullet is given by shock waves. These are thin, not isentropic<sup>2</sup> regions of high density, temperature, pressure and velocity gradients. They are formed when the gas flows at a speed greater than the speed of sound of the medium which creates a discontinuity. This discontinuity creates the "Mach Disk" as shown in Figure 1.6. The shock waves reduce the velocity of the gas flow and the Mach number to subsonic values.

<sup>&</sup>lt;sup>2</sup>Isentropic flow: A type of flow process that is regarded as reversible and adiabatic, i.e. no heat transfer or energy dissipation between the fluid and its surroundings. It is the typical flow process of a gas when it passes through a nozzle.

The gas undergoes an isentropic expansion initially. However, it is not aware of the background pressure and the increasing Mach number. As a result, it overexpands, which means that it has to be recompressed. This is possible with the help of the barrel shock at the sides and the Mach disk shock which is perpendicular at the centerline.

The "zone of silence" is a region in which an isentropic expansion takes place. It does not depend on the background pressure and is not influenced by any external conditions. Inside this region, we can place a skimmer in order to retrieve the centerline beam. The skimmer is placed in front of the reservoir (nozzle) and before the Mach Disk where the flow collapses. The Mach disk location,  $x_m$ , depends on the diameter of the nozzle and is given by the following relation

$$\frac{x_m}{d} = 0.67(\frac{P_0}{P_b}) \tag{1.38}$$

## 1.5 Ion Imaging

Ion imaging is a technique combining time-of-flight mass spectrometry and positionsensitive detection to measure simultaneously the kinetic energy and spatial distribution of charged particles. In this thesis we are using a version of the technique called Velocity Map Imaging as will be explained below.

## **1.5.1 Imaging History**

Chandler and Houston<sup>7</sup> published their novel work in 1987. They presented a groundbreaking way of measuring the three-dimensional spatial distribution of a photofragment, namely  $CH_3^+$ , by projecting its Newton sphere onto a two-dimensional surface. The molecule under study was  $CH_3I$ , which was photolyzed by a Nd:YAG laser beam of 266 nm and a dye laser system at 330 nm (frequency-doubled) that interacted with the molecular beam within a 10 ns timeframe. Furthermore, their experimental setup consisted of a repeller (0-250 V) which created a uniform electric field, two grounded grids and an ion shutter that was in front of the Position-Sensitive Detector (PSD). The components of the PSD were a microchannel plate coupled to a phosphor screen an a CMOS camera. As soon as the methyl cation radical passed through, the ion shutter was activated at 250 V in order to separate the fragments. Although revolutionary at that period of time, the large size of the laser-molecular beam interaction region limited energy resolution.

Eppink and Parker<sup>8</sup> published their work in 1997, greatly enhancing the technique proposed by Chandler and Houston. Their setup consisted of a repeller, an extractor and a ground electrode, which make up an electrostatic lens. A laser beam interacts with the molecular beam. Using electrostatic lenses, the fragments hit the same exact position on the detector if they have the same velocity, without taking into consideration where they were produced in the laser-molecular beam interaction region. This is the reason why the technique is called "Velocity Map Imaging". This work greatly improved the resolution of energy to 1-5%. However, there is still the need to calibrate the kinetic energy release and perform the inverse Abel transform.

Gebhardt *et al.*<sup>9</sup> introduced an improvement of the Velocity Map Imaging technique called Slice Imaging. The need to use the inverse Abel transform to obtain the 3D distribution from its 2D projection, introduces significant noise in the kinetic energy and angular distribution results. The Slice Imaging technique eliminates the need for the inverse Abel transform. After a period of free field expansion, a pulsed electric field is

applied to the expanding ion sphere. As a result, and with the use of a probe time gate of several nanoseconds, the authors were able to record the central region of the ionic cloud. This region holds enough information that is otherwise found in the inverse Abel transform. Compared to the VMI technique, the Slice Imaging technique energy resolution capabilities are equal to the VMI ones.

Townsend *et al.*<sup>10</sup> reported an alternative to the Slice Imaging technique called "Direct Current Slice Imaging". In this method, the ion cloud was accelerated by a weak field in the interaction region, which formed the temporal spread. Shortly after, the ionic sphere was subjected to a strong field which utilized the VMI technique.

Papadakis and Kitsopoulos<sup>11</sup> managed a notable reduction in the electostatic lens proposed by Eppink and Parker. Their setup was just two electrodes, giving rise to a single-field of acceleration. This was accomplished by introducing a minor modification to the repeller (protrusion) and grounding the extractor. The result was a resolution of  $\sim 1\%$  in velocity.

#### 1.5.2 Time-of-Flight Mass Spectrometry

Time-of-Flight Mass Spectrometry is an analytical technique that separates the charged particles or ions that are produced through the interaction of the molecular beam with radiation, e.g. a laser beam. The separation is based on the mass-to-charge ration m/z of the produced radical ions.

After the ionization of the molecule, the ions are accelerated by an electric field. As the ions pass the extractor, they reach the time-of-flight tube, where the velocity of each ion can be found since we know that their energy is related to the strength of the electric field

$$E = qV \tag{1.39}$$

where V is the electric potential energy. The energy of the ion is converted into kinetic energy, so

$$\frac{1}{2}mv^2 = qV \tag{1.40}$$

Solving in terms of the velocity, we get

$$v = \sqrt{\frac{2qV}{m}} \tag{1.41}$$

Throughout the length of the flight path, the velocity of each ions remain intact since they traverse through a field-free path and the ions are separated. It is obvious from Eq. 1.41 that the lighter the mass, the higher the velocity. As a result, the lighter ions reaches the detector first, with the other ions reaching the detector in different times with respect to their mass. The time  $t_{ToF}$  that each ion reaches the detector is given by the formula

$$t_{ToF} = d\sqrt{\frac{m}{2qV}} \tag{1.42}$$

and since q=ze, we get

$$t_{ToF} = \frac{d}{\sqrt{2eV}} \sqrt{\frac{m}{z}} \tag{1.43}$$

where  $\frac{m}{z}$  is the mass-to-charge ratio. As an example, we can consider the case of photodissociation of bromoform. Assume that after the interaction of the molecular beam

with the laser one, we get  $H^+$ ,  $C^+$ ,  $CH^+$ ,  $CHBr^+$  and  $CHBr_3^+$ . The ions will show on the oscilloscope (see 2.1.5) in this exact order, since they follow a lighter-to-heavier mass ratio.



Figure 1.7: Time-of-Flight Mass Spectroscopy Schematic

### 1.5.3 Newton Spheres

Each photoionization (Eq. 1.1) and photodissociation (Eq. 1.2) produces a pair of fragments, each respecting the conservation of energy discussed in section 1.2.1 and flying in opposite directions. If we reiterate the same process many times, the fragments build up spherical distribution in velocity space. These are the Newton spheres for the process.

Suppose that we have process  $AB + 1hv \rightarrow A + B$ , where  $m_A < m_B$ . Assuming that only one event takes place (Event 1, although a myriad of events may occur), we can see the two Newton spheres that are formed, the green one for fragment B and the red one for fragment A, shown in the following figure



Figure 1.8: Newton Spheres for the process, Event 1 is for fragment A and Event 1' is for fragment B.

For a given process, a certain mass will have the same exact velocity. As a result, it will produce a Newton sphere and every particle will eventually fall somewhere along it. For example, Event 1 in Figure 1.8 describes the Newton Sphere that fragments A will produce. Newton Sphere A is larger than Newton Sphere B due to the fact that it is lighter which leads to a velocity greater than that of fragment's B. As a result, the size of a Newton sphere is directly proportional to the fragments' speed. Furthermore, the final position of a fragment depends on the it's velocity. It is obvious that in the first occasion the quantity is a scalar (speed), while in the second it is a vector (velocity). We can record the 3-D Newton sphere by getting its 2-D projection on a camera. The result will be a partially filled-in circle. With the use of mathematics and computer programs (see section 2.1.6), we can recover the 3-D information.

#### 1.5.4 Velocity Map Imaging

As mentioned above, Eppink and Parker published their work which took the name "Velocity Map Imaging". This is the technique that we used for the present thesis. It revolutionized the research in the molecular dynamics field. The schematic of the technique can be shown in Figure 1.7. The creation of the Newton sphere takes place pretty close to the extractor, i.e. the photoionization. The repeller and the extractor electrodes form a non-homogeneous electric field. The electrodes act as an electrostatic lens and do not have any grids, which is the reason for the formation of such a field. The magnification factor of the lens can be found either by simulations of the trajectories of the ions or photoelectrons or by experiment. The produced particles' trajectories with initial velocity  $|u_x|$ ,  $u_y$ ,  $u_z$  reach the same spot on the lens focal plane which is the detector. Ions of the same mass with the same velocity hit the same point on the detector independent of the origin of formation, thus the name Velocity Map Imaging.

The VMI experiment consists of four steps:

- 1. Photodissociation forms the Newton spheres. The laser beam is linearly polarized with the polarization vector parallel to the detector plane and perpendicular to the molecular beam.
- 2. Photoionization of the photofragments
- 3. 2-D projection of the 3-D ionic cloud onto the detector.
- 4. Utilization of the inverse Abel transform on the 2-D projection in order to obtain the 3-D information.



Figure 1.9: Schematic of a repeller-extractor setup

# **Chapter 2**

# **Experimental Setup**

## 2.1 The Apparatus

It is generally acknowledged that the higher the vacuum, the better in terms of imaging ions and photoelectrons. In other words, a high vacuum is needed in order to avoid collisions between the molecule in study and other molecules present in the chamber that would distort the energy distribution of the fragments, as well as their angular distributions. The experimental setup that was used is shown in Figure 2.1.



Figure 2.1: 2D representation of the VMI experimental setup

The apparatus consists of the source chamber and the detection chamber. The two chambers will be briefly discussed in the following subsections.

#### 2.1.1 The source chamber

The source chamber is the first of the two chambers. This is where the molecular beam is produced through a nozzle valve. The source chamber is pumped by a baffled diffusion pump (Leybold DI3000,  $3*10^3$  lt/s). The pressure in the chamber is  $\sim 10^{-6}$  Torr. There is also a rotary mechanical oil pump (Leybold Trivac D65B, 65 m<sup>3</sup>/h), which provides a backing pressure of about  $10^{-3}$  Torr. The source chamber is separated from the detection

chamber with a skimmer ( $\emptyset$ =1.5 mm). One benefit of this approach is that we can achieve a higher vacuum in the detection chamber and have a collimated molecular beam.

## 2.1.2 Gas handling system

The gas mixtures were made in a gas handling system that includes a glass u-tube setup (Figure 2.2). The tube was filled with cotton throughout its length because both molecules were in liquid phase in room temperature.



Figure 2.2: The bubbler

The intake was connected to a He tank, whereas the exit was connected to the nozzle with a Teflon tube. When the molecule to be studied was inserted into the glass gas handling system, it was absorbed by the cotton, thus, having He flow, the gas molecule was pushed along towards the nozzle and from there to the chamber.



Figure 2.3: The gas handling system that was used in the experiment

## 2.1.3 Nozzle

The nozzle or pulse valve ( $\emptyset$ =0.8 mm) that was used in the experiment is a home-made piezoelectric one, operating at 10 Hz, which is based on the design of Proch and Trickl. The nozzle has a small aperture, that allows the gas mixture to go from atmospheric to source chamber pressure, about 10<sup>-6</sup> Torr. The aperture is sealed with an o-ring. This allows the nozzle system to be sealed when there is no gas flow, whereas when we apply voltage to the piezoelectric crystal, because of its retraction, the gas flows towards the chamber due to the fact that the aperture opens. The gas enters the chamber with the help of a Teflon tube which is connected to the nozzle. Furthermore, the crystal is operated with an applied voltage of 800 V. Just ~ 1 cm in front of the nozzle, there is the skimmer, which was mentioned above.



Figure 2.4: The nozzle and the skimmer

## 2.1.4 Detection Chamber

The detection chamber is pumped by a turbo-molecular pump (Pfeiffer HiPace 700, 655 Lt/sec), which achieves a pressure of about  $10^{-7}$  Torr. A rotary mechanical pump (Leybold Trivac D25B, 25 m<sup>3</sup>/h) provides the backing pressure that is about  $4 * 10^{-3}$  Torr.



Figure 2.5: The apparatus of the VMI experiment.

The laser beam goes through the detection chamber through the two quartz windows that are present on the sides of the chamber, thus it is perpendicular to the molecular beam. The two beams interact with each other and ions are produced. These ions are headed towards the detector through a system of electrostatic optics. These consist of a repeller and an extractor plate that feature protrusions in order to form an inhomogeneous electric field. The interaction of the two beams happens between the repeller and the extractor. The repeller is usually at 4kV, whereas the extractor is grounded. After the interaction and the production of ions, these ions have a 45 cm free region TOF (Time of Flight) before they arrive at the detector.



Figure 2.6: Schematic of the repeller-extractor setup

The detector is home-build and consists of two parts, the first being two Micro Channel Plates (MCPs) (BASPIK,  $\emptyset = 50$ cm, Channel diameter =  $12 \ \mu m$ ) and the second being a Phosphor plate (Proxitronix, P47,  $\emptyset = 40$  mm). For one electron hitting the MCP,  $10^6$  secondary electrons are emitted. We can see how a Phosphor plate works, as well as an image of a MCP in Figure 2.7. These MCPs cannot detect neutral radicals/ particles unless their internal electronic energy is above 5 eV<sup>5</sup>. In order to detect them, they must be ionized. During this conversion process the velocity of the neutral particle must remain the same in order to have all excess TKER absorbed by the electron.



Figure 2.7: Micro Channel Plate

## 2.1.5 Oscilloscope & Ion Images

As soon as the secondary electrons are emitted, they hit the phosphor plate, thus emitting photons. These photons reach the CMOS camera (Unibrain i702b). On the oscillator (Hameg Instruments, Analog Digital Scope, HM1507-3, Figure 2.8) we can see the different peaks of the spectrum.



Figure 2.8: Hameg Instruments Oscilloscope

These peaks are basically the ions with different m/z ratios, i.e  $H^+$  will be the first thing we can see, whereas the ion of the parent molecule will be on the far right of the spectrum.

When we want to take an image of an ion, we image only the said ion through a process called gating. In this mode, the repeller has a voltage of 4 kV, MCP Gate is switched on at 700 V (whereas it is off when we are not doing the said process), MCP Back at 1.2 kV and the Phosphor at 6 kV. We also modify the time delay of the laser from the pulse generator (BNC Model 565 Pulse/Delay Generator, Figure 2.9).



Figure 2.9: BNC Pulse Generator

When both beams are on, we can see what happens in real time with the help of a program that is responsible for connecting the camera with the computer. Usually we take 400 frames for each ion image, with the total amount of images being 10. Moreover, we take images for the background, i.e. the molecular beam is switched off and the laser beam is on, 400 frames of each background image and a total amount of 5 images. An example of an ion image is shown in Figure 2.10.

## 2.1.6 The programs for the analysis

The camera records an image that is the projection of the ionized photofragments' sphere. The laser polarization is parallel to the detector plane (i.e. in the y-axis in the laboratory system of reference,  $\hat{\varepsilon} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ ). Furthermore, the polarization manipulates the ion sphere to have a cylindrical symmetry. Every row in the projection of the sphere is the projection of a circle.

#### **1.** Center of the sphere

For each ion, we add every image taken for the ion and subtract every background. Having produced the image, we try to find the center of the ion image. We used Adobe Photoshop Version: 13.0.1 in order to view the images. Taking a small range on the x and y axes and use two programs that take intensity histograms through the image, we were able to find the exact center of the sphere. The center is later utilized in the following steps of the analysis.





#### 2. Quadrant Averaging

Having found the center of the image, we need to make a quadrant averaging in order to subtract any noise that may be present in our image in each pixel and outside the rings. The result is an image perfectly symmetrical (as in Figure 2.11). This symmetry is crucial because of the Abel transformation.



Figure 2.11: Figure of CH<sub>3</sub>I after performing the flip program

#### 3. Abel Transform

Let F(r) be the function of the circle discussed above, then the 2D projection f(x) of the circle, i.e. a line, on the  $\hat{x}$ -axis is given by Equation 2.1

$$f(x) = 2 \int_{x}^{\infty} \frac{F(r)rdr}{\sqrt{r^{2} - x^{2}}}$$
(2.1)

Ions of different kinetic energy are projected on the detector as concentric circles. In order to reconstruct the radially symmetric 2D function (circle) from the 1D projection, meaning the line (f(x)), we use the inverse Abel transformation with the use of a Fourier transform of f(x) followed by a Hankel transformation. The final formula for F(r) is

$$F(r) = \frac{1}{\pi} \int_{r}^{\infty} \frac{df(x)}{dx} \frac{dx}{\sqrt{x^2 - r^2}}$$
(2.2)

F(r) is calculated through the use of the Abel transformation of an image and is sensitive to noise and asymmetries, as it is obvious in Figure 2.12 and in Equation 2.2, where in the limit of  $r \rightarrow x$  the integral blows up to infinity.

The program performs this above per line. It produces a picture in which every line is the section of the circle. In other words, we apply the inverse Abel transformation in order to get a 2D section of the 3D Newton sphere. The sum of all these circles forms a section on the sphere.

#### 4. Intensity - KER graphs

As soon as we have the images from the abel program, we can integrate the images over  $\phi$  from 0 to  $\pi$ . Then, we can plot the intensity of the image versus the radius. Since the radius is in pixels, and we know the relation between kinetic energy and pixels, we can plot the Intensity-KER graph and analyse our data, that is finding the dissociation channels that happened during the interaction of the two beams. More information is provided in section 2.3 of this chapter.



Figure 2.12: CH<sub>3</sub>I after the Abel transformation

## 2.2 Laser and Alignment

## 2.2.1 Laser

The laser used in the experiment was an ArF-based excimer laser at 193 nm. It was operating in external mode and connected to channel F on the pulse generator, with a frequency of 10 Hz. Thus, we could manipulate the delay between the laser and the molecular beam in order to optimize the signal of a given ion. The laser power was  $\sim 60$  mJ/pulse at 26 kV, whereas after the alignment and right before its entry into the chamber was  $\sim 0.4$  mJ/pulse.



Figure 2.13: The ArF laser that emits at 193 nm

## 2.3 Calibration of the Kinetic Energy Release

The detector measures the intensity in arbitrary units per pixel. In other words, the result that we get is the number of photofragments per pixel. It is known that the kinetic energy of a photofragment is proportional to the pixels squared, i.e.

$$K = A (pixel)^2$$
(2.3)

where K is the kinetic energy and A is the calibration factor. This factor A has to be known in order to calculate the energies of all the photofragments that we measured in the laboratory, such as  $C^+$  and  $CH^+$ .

We chose CH<sub>3</sub>I for our reference system, since its photodissociation process is extensively studied. The dissociation bond energy of CH<sub>3</sub>I is 2.33 eV<sup>12</sup>. We utilized the other laser that is present in the Chemical Dynamics Laboratory. It is dye laser system (LPD3000, Coumarin 102), pumped by an excimer laser (Lambda Physik LPX, XeCl). As for the doubling of the frequency, we used a BBO crystal. The excitation energy was equal to 41275.3 cm<sup>-1</sup>, where E(1hv) = 5.12 eV and the wavelength was 242 nm after the doubling. Thus, the process is the following

$$CH_3I + 1hv \longrightarrow CH_3 + I({}^2P^0_{1/2})$$
(2.4)

The total kinetic energy release is equal to

TKER = 
$$E(1hv) - D_0 = 2.787392763 \text{ eV}$$
 (2.5)

where most of the energy is attributed to the methyl radical (2.49 eV), and the other to the Iodine (0.29 eV). Knowing the energy of the Iodine, we can calculate the calibration factor A, since we can find the 'pixel' term in equation 2.3 from the graph below.



Figure 2.14: Intensity - Pixels graph for Iodine at 4kV

Knowing the 'pixel' term, we calculate the calibration factor to be  $A = 3.599 \times 10^{-6} \text{eV}/\text{pixel}^2$ . In Figure 2.15, we can see the energies on the x-axis.



Figure 2.15: Intensity - Energy graph for Iodine at 4kV

We can see that our calibration factor works, since taking the value where there are no vibrations, that is on the end of the curve, is 0.29 eV, which is the same as the theoretical calculation above. Knowing A, we can proceed with the analysis for the two other molecules.

# **Chapter 3**

## Photodissociation of CH<sub>2</sub>Br<sub>2</sub> at 193 nm

### 3.1 Introduction

 $CH_2Br_2$  is the chemical formula for dibromomethane or methylene bromide. It was discovered by German chemist Justus von Liebig in 1832. He synthesized dibromomethane by treating  $CH_2Cl_2$  with Br. It adopts a tetrahedral molecular geometry with  $C_{2\nu}$  symmetry. Its molecular weight is 173.835 g/mol. In the next two figures (3.1), we can see dibromomethane in 2D and 3D representations.



Figure 3.1: Dibromomethane in a) 2D and in b) 3D representations

It is an organobromide compound, which is produced naturally by marine algae<sup>13,14</sup>. It can also be produced by synthesis. Moreover, it can be used as a solvent, is not soluble in water and can be used as motor fuel. It is a clear, colorless liquid with pleasant smell. Dibromomethane density is 2.477 g/cm<sup>3</sup>, making it denser than water<sup>15</sup>. The hybridization of the core atom C is sp<sup>3</sup>.

 $CH_2Br_2$  has attracted the attention of many scientists. From the field of atmospheric chemistry<sup>16,17</sup>, to that of environmental science<sup>18</sup>, it is a molecule that has been studied a lot. Since the late 1990s and early 2000s, dibromomethane is a molecule that has been a research topic in the field of photochemistry.

Huang *et al.*<sup>19</sup> studied the photodissociation of  $CH_2Br_2^+$  using the Velocity Map Imaging technique at 355 nm, which was produced after the interaction of the neutral molecule with a pulsed 118 nm laser. They report that the dissociation of  $CH_2Br_2^+$  can happen if the ion absorbs another 355 nm photon. The formed  $CH_2Br^+$  is highly vibrationally excited whereas the Br atom can be either in the ground ( ${}^2P_{3/2}$ ) or in the spin-orbit excited state ( ${}^2P_{1/2}$ ), with a 1.0:2.2 branching ratio .

Lee *et al.*<sup>20</sup> presented the photodissociation of  $CH_2Br_2$  at 248 nm through the use of product translational spectroscopy. Dibromomethane goes through a simple C-Br bond fission. A secondary photodissociation of  $CH_2Br$  produces another Br, although it is not stated if it is in ground or spin-orbited state.

Chiang *et al.*<sup>21</sup> published a paper where they ionized  $CH_2Br_2$  molecules with monochromatic vacuum UV radiation at 60 nm. They report an experimental ionization energy of  $10.25 \pm 0.02$  eV for CH<sub>2</sub>Br<sub>2</sub>, 8.47 eV for CH<sub>2</sub>Br, 9.02 eV for CHBr and 8.55 eV for CBr. Yang *et al.*<sup>22</sup> utilized laser-induced dispersed fluorescence in order to obtain spectra

From the multiphoton photodissociation of  $CH_2Br_2$  at 266 nm. The first two dissociation channels are those where the two bromines are separated and  $CH_2$  is in its ground triplet state  $(\widetilde{X^3}B_1)$ , although not observed by their experimental setup. The third photon dissociates  $CH_2$  to generate an electronically excited CH ( $A^2\Delta$ ) radical.

Long *et al.*<sup>23</sup> reported mass-resolved (2+n) REMPI data for  $CH_2Br_2$  with the use of an dye laser system pumped by an excimer laser that emitted in the range of 480 to 560 nm. Using a BBO crystal, they were able to receive the 2-photon resonance excitation region from 71200 to 82300 cm<sup>-1</sup>. They detected signals of H<sup>+</sup>, C<sup>+</sup>, CH<sup>+</sup>, CH<sup>+</sup>, CH<sup>+</sup>,  $^{79}Br^+$  and  $^{81}Br^+$ . The two-photon resonance transitions to molecular Rydberg states are responsible for the structure observed in the spectra of all the ions except H<sup>+</sup>.

In this chapter, we present results of VMI experiments fpllowing photoexcitation of  $CH_2Br_2$  at 193 nm.

## 3.2 The experiment

As discussed in section 2.1.2,  $CH_2Br_2$  was in liquid phase during the experiment. The experiment involved inserting the molecule in the bubbler (Figure 2.2). By modifying the voltage applied to the crystal, we could adjust the gas flow rate that was inserted into the chamber by checking the pressure values of the Pirani and Penning gauges. Throughout the experiment, we adjusted the He intake so that the pressure shown in the manometer of Figure 2.3 was kept constantly at 0.8 bar.

The ArF laser that was used in the experiment operates at 193 nm. The laser beam inserts the detection chamber through the quartz window that is present on the left, as seen on the left of Figure 2.5. The laser beam was polarized by reflection, right after exiting the laser, by a quartz window at Brewster angle. The polarization was parallel to the detector. Furthermore, we utilized a system of three reflective mirrors and a converging lens with focal length of 5 meters to get the laser beam to the VMI setup. Right before the beam enters the detection chamber, there is another converging lens with focal length of 20 centimeters. A 2D schematic of the alignment can be seen in Figure 3.2 below



Figure 3.2: 2D representation of the alignment

Adjusting the second converging lens, as well as the nozzle-laser pulse delay using the BNC Pulse Generator, we were able to maximize the signal shown in the oscilloscope.

The photofragments that we recorded using Velocity Map Imaging were C<sup>+</sup>, CH<sup>+</sup>, CH<sub>2</sub><sup>+</sup>, Br<sup>+</sup>, CH<sub>2</sub>Br<sup>+</sup> and the parent ion, i.e.  $CH_2Br_2^+$ . We could not image H<sup>+</sup> due to its high velocity, meaning that it was out of range of the position sensitive detector.

## 3.3 Results

## 3.3.1 Photofragment & Photoelectron Images

In the following figure, I present the photofragment images of the ions that we recorded. The ions are presented from lighter to heavier mass.



Figure 3.3: The recorded ions

The laser is polarized on the  $\hat{y}$ -axis. Thus, C<sup>+</sup> has a perpendicular transition, whereas CH<sup>+</sup> and CH<sub>2</sub><sup>+</sup> a parallel transition. Furthermore, the photoelectrons that we recorded for dibromomethane are shown below.



Figure 3.4: Photoelectrons of CH<sub>2</sub>Br<sub>2</sub>

The photoelectrons do not have any clear rings. Most of the signal that forms is the one in the center, which is due to the ionization of the parent molecule.

Since the electrons have zero kinetic energy, this means that the energy was distributed into high vibrationally excited states, as presented in the next figure.



Figure 3.5: PES of the photoelectrons

The energy left after the ionization is close to zero. The same process happens for all the other molecules' ionization.

### 3.3.2 KER distributions

In this subchapter, I will present the KER distributions (Intensity (A.U.) versus Kinetic Energy Release(KER)(eV)) of the ions shown in Figure 3.3.

### $CH_2Br^+$

The only process that occurs is the one where dibromomethane is excited with 2 photons, leading to its ionization and then the ionized parent molecule's dissociation (simultaneously). Due to the fact that  $CH_2Br_2$  is a large molecule, we can assume that there are more than one vibrational modes excited. This is obvious particularly by process 3.5, where the  $CH_2Br^+$  radical has a combination of modes, four in total. From all of these different combinations, we not only see  $CH_2Br^+$ , but also Br, which will be presented in the graph below.

The scenario of the dissociation of  $CH_2Br_2$  into  $CH_2Br$  and Br was studied. The bond dissociation energy of this reaction is  $D_0(CH_2Br - Br)=2.86 \text{ eV}$ , meaning that one photon is required and the energy distributed to the two fragments is  $E(CH_2Br)=1.63 \text{ eV}$  and E(Br)=1.93 eV. In order to have values that fit the KER,  $CH_2Br$  would have to be highly vibrationally excited (v > 9). Besides that, two more photons are needed in order to ionize

the radical, greatly lowering the probability of this process. Moreover, we do not observe photoelectrons from  $CH_2Br$  ionization (only near-zero/ZEKE photoelectrons) that would indicate formation of CH2Br fragments.

After absorbing two photons,  $CH_2Br_2$  receives enough energy to be ionized. The available energy after the ionization is enough to lead to the bond rupture between  $CH_2Br^+$  and Br. We show four of the many vibrational energy distribution scenarios in processes 1-4 below and in Figure 3.6.



Figure 3.6: KER of  $CH_2Br^+$ 

1) 
$$\operatorname{CH}_2\operatorname{Br}_2 + 2\operatorname{hv} \longrightarrow \operatorname{CH}_2\operatorname{Br}^+(v_4 = 9, 10) + \operatorname{Br} + e^-$$
 (3.1)

2) 
$$CH_2Br_2 + 2hv \longrightarrow CH_2Br^+(v_2 = 2, 3, v_4 = 1, v_{4'} = 1, v_5 = 2) + Br + e^-$$
 (3.2)

3) 
$$CH_2Br_2 + 2hv \longrightarrow CH_2Br^+(v_4 = 1, v_5 = 3) + Br + e^-$$
 (3.3)

4) 
$$CH_2Br_2 + 2hv \longrightarrow CH_2Br^+(v_2 = 7,8) + Br^* + e^-$$
 (3.4)

The frequencies of vibrational modes of CH<sub>2</sub>Br<sup>+</sup> are:

- $v_2 \rightarrow \text{CBr str.} (876 \text{ cm}^{-1})$
- $v_{4'} \rightarrow CH_2 \text{ wag } (1024.7 \text{ cm}^{-1})$
- $v_4 \to CH_2 \text{ wag } (1084 \text{ cm}^{-1})$
- $v_5 \rightarrow CH_2 \text{ a-str} (3127.9 \text{ cm}^{-1})$

#### <u>Br</u>+



For the Bromine ion, we get the following KER distribution shown

Figure 3.7: Br<sup>+</sup>

Bromine is the second heaviest ion that we recorded. Its KER has a maximum value of about 0.09 eV. The processes that describe the KER of  $CH_2Br_2$  describe that of bromine as well. The fact that in these processes the  $CH_2Br^+$  received the positive charge means that Br has to be ionized with the help of two photons, since its ionization potential energy is 11.81 eV. The same thing occurs when  $CH_2Br^+$  absorbs one photon and dissociation into  $CH_2^+$  and Br ( $D_0(CH_2^+ - Br)=5.55$  eV). Since we do not have photoelectrons corresponding to these processes, we conclude that they are less likely to happen.

Another reaction that could be possible is the one where  $CHBr^+$  dissociates into CH and  $Br^+$ . First of all,  $CH_2Br$  would have to break into CHBr and H. The fact that we did not record any images of CHBr or H means that it could be produced but in a such a small quantity making it difficult to detect. As a result, we can disregard this channel.

Bromine has the most processes of all the ions. These are:

1-4) 
$$CH_2Br_2 + 2hv \longrightarrow CH_2Br^+$$
 (rovibrationally excited) + Br/Br\* + e<sup>-</sup> (3.5)

5) 
$$\operatorname{CH}_2\operatorname{Br}^+ + \operatorname{1hv} \longrightarrow \operatorname{CH}_2^+(v_2 = 4 - 7) + \operatorname{Br}$$
 (3.6)

6) 
$$\operatorname{CH}_2\operatorname{Br}^+ + \operatorname{1hv} \longrightarrow \operatorname{CH}_2^+(v_2 = 4 - 7) + \operatorname{Br}^*$$
 (3.7)

7) 
$$\operatorname{CH}_2\operatorname{Br}^+(v_2=2) + 1\operatorname{hv} \longrightarrow \operatorname{CH}_2 + \operatorname{Br}^+$$
 (3.8)

8) 
$$\operatorname{CH}_2\operatorname{Br}^+ + 1\operatorname{hv} \longrightarrow \operatorname{CH}_2^+(v_3 = 1, 2) + \operatorname{Br}$$
 (3.9)

The vibrational modes used in these processes are

- For  $CH_2Br^+$ :  $v_2$  (CBr str., 876 cm<sup>-1</sup>),  $v_{4'}$  (CH<sub>2</sub> wag, 1024.7 cm<sup>-1</sup>),  $v_4$  (CH<sub>2</sub> wag, 1084 cm<sup>-1</sup>),  $v_5$  (CH<sub>2</sub> a-str., 3127.9 cm<sup>-1</sup>)
- For  $CH_2^+$ :  $v_2$  (bend, 968.4 cm<sup>-1</sup>),  $v_3$  (CH a-str., 3131.37 cm<sup>-1</sup>)

The processes that explain the KER of the  $CH_2Br^+$  also explain some part of the spectrum shown in this subsection. Besides these, four more processes take place. More specifically,  $CH_2Br^+$  absorbs one photon and produces  $CH_2^+$  and Br (two processes with different vibrational modes) or the spin-orbit excited Br\*. In the other process, Br receives the positive charge and the methylene radical remains neutral.

### $\mathbf{CH}_2^+$

Since dibromomethane has one carbon, two hydrogen and two bromine atoms, the only processes that can produce the methylene radical are the ones where the radical has one bromine and dissociates into  $CH_2^+/CH_2$  and  $Br/Br^+$ .



Figure 3.8:  $CH_2^+$ 

Four processes occur for  $CH_2^+$ . These are:

5) 
$$\operatorname{CH}_2\operatorname{Br}^+ + \operatorname{1hv} \longrightarrow \operatorname{CH}_2^+(v_2 = 4 - 7) + \operatorname{Br}$$
 (3.10)

6) 
$$\operatorname{CH}_2\operatorname{Br}^+ + 1\operatorname{hv} \longrightarrow \operatorname{CH}_2^+(v_2 = 4 - 7) + \operatorname{Br}^*$$
 (3.11)

7) 
$$\operatorname{CH}_2\operatorname{Br}^+(v_5=2) + 1\operatorname{hv} \longrightarrow \operatorname{CH}_2 + \operatorname{Br}^+$$
 (3.12)

8) 
$$\operatorname{CH}_2\operatorname{Br}^+ + \operatorname{1hv} \longrightarrow \operatorname{CH}_2^+(v_3 = 1, 2) + \operatorname{Br}$$
 (3.13)

with the vibrations being

- For  $CH_2Br^+$  :  $v_5$  ( $CH_2$  a-str., 3127.9 cm<sup>-1</sup>)
- For  $CH_2^+$ :  $v_2$  (bend, 968.4 cm<sup>-1</sup>),  $v_3$  (CH a-str., 3131.37 cm<sup>-1</sup>)

These processes explain the spectrum  $CH_2^+$ , as well as a large part of the Br graph. As a result, almost all of this spectrum is described by the  $CH_2^+$  fragment, where the one olive vertical line is that of  $CH_2$ .

### $\underline{\mathbf{C}\mathbf{H}^+}$

The next graph is that of CH<sup>+</sup>. It can be produced by  $CH_2^+/CH_2$  or by CHBr<sup>+</sup>/CHBr. The second option has been mentioned above, so we will not refer to it here. As a result, the only option for the production of the methylene radical is the neutral or the CH<sub>2</sub> ion.



Figure 3.9: CH<sup>+</sup>

Three processes explain the spectrum. These are

9) 
$$\operatorname{CH}_{2}^{+} + 1\operatorname{hv} \longrightarrow \operatorname{CH}^{+}(v_{1} = 0 - 5) + \operatorname{H}$$
 (3.14)

10) 
$$CH_{2}^{+}(v_{2} = 1 - 6) + 1hv \longrightarrow CH^{+} + H$$
 (3.15)

11) 
$$CH_2 + 1hv \longrightarrow CH(v_1 = 0 - 5) + H$$
 (3.16)

where

- For CH<sup>+</sup> :  $v_1$  (X<sup>1</sup> $\Sigma^+$ , 2558 cm<sup>-1</sup>)
- For CH :  $v_1$  (X<sup>2</sup> $\Pi_r$ , 2858.5 cm<sup>-1</sup>)

Almost the whole graph is explained by processes 3.14 and 3.15. As a result, CH<sup>+</sup> is the main reason for this explanation, whereas CH can explain only the first half of the graph.

### $\underline{\mathbf{C}^+}$

The graph of  $C^+$  is shown below



Figure 3.10: C<sup>+</sup>

In these processes, the reactant is in a given vibrational mode. Due to the fact that we did not record an image for hydrogen, we have to take into consideration only the values that we get for carbon.

We could get the carbon ion from the dissociation of CBr, but we do not have any indications that such a pathway would work since it would need first to have CHBr or CBr<sub>2</sub>, both of which not showing anywhere in the KER distributions we have presented.

As in CH<sup>+</sup>, this KER distribution can be described by three processes, these being

12) 
$$CH^+(v_1 = 0 - 6) + 1hv \longrightarrow C^+ + H$$
 (3.17)

13) 
$$CH^+(v_1 = 1 - 6) + 1hv \longrightarrow C + H^+$$
 (3.18)

14) 
$$CH(v_1 = 0 - 5) + 1hv \longrightarrow C + H$$
 (3.19)

where

- For CH<sup>+</sup> :  $v_1$  (X<sup>1</sup> $\Sigma^+$ , 2558 cm<sup>-1</sup>)
- For CH :  $v_1$  (X<sup>2</sup> $\Pi_r$ , 2858.5 cm<sup>-1</sup>)

#### 3.3.3 Discussion

In general, the processes that most probably take place in the photodissociation of  $CH_2Br_2$  are shown in the next diagram.



Figure 3.11: The processes of CH<sub>2</sub>Br<sub>2</sub>'s photodissociation

Following the analysis of the ions, it is obvious that the most plausible channels are three. All three of them start from the same process, that is two photons ionize and dissociate  $CH_2Br_2$  into  $CH_2Br^+$ , Br/ Br\* and e<sup>-</sup> simultaneously. Since the energy of one photon is 6.42 eV, the ionization potential energy of  $CH_2Br_2$  is 10.41 eV and

 $D_0(CH_2Br^+ - Br) = 1.06 \text{ eV}$ , the available energy after the ionization and then the dissociation is ~1.37 eV. Utilizing the formulas found in Eq. 1.8, we get the following energies for the fragments:  $E(CH_2Br^+)=0.63 \text{ eV}$ , E(Br)=0.74 eV and if we have the excited state of bromine(~0.46 eV above the ground state), Br\*, we get  $E(CH_2Br^+)=0.92 \text{ eV}$  and  $E(Br^*)=0.49 \text{ eV}$ . Thus, the products must have internal energy, i.e. vibrations and rotations, since the maximum kinetic energy release we have in graph 3.6 of  $CH_2Br^+$  is ~0.15 eV and in the bromine graph is ~0.87 eV. The internal energy of the products is shown in equations 3.5-3.4 and 3.5-3.13, respectively. The same procedure is applied to all processes.

In the first one, the  $CH_2Br^+$  radical dissociates into  $CH_2^+$  and  $Br/Br^*$ , with the help of one photon  $(D_0(CH_2^+ - Br)=5.55 \text{ eV})$ . Following that, one photon breaks the bond of  $CH_2^+$  into  $CH^+$  and H. This dissociation is more possible than that of  $CH_2^+$  into  $CH + H^+$  $(D_0(CH^+ - H)=4.62 \text{ eV})$  because it needs one photon to happen, whereas the process where the bond breaks into neutral methylidyne radical and ionized hydrogen needs two photons in order to have an available energy greater than zero. As a result of the dissociation processes 3.14 and 3.15, one photon is enough to dissociate  $CH^+$  into  $C^+$  and H  $(D_0(C^+ - H)=4.09 \text{ eV})$  or into C and  $H^+$   $(D_0(CH_2^+ - Br)=6.43 \text{ eV})$ . We believe the first process occurs with higher probability, as we had very low H+ signal on the scope and we could not record a clear image of it. Furthermore, if the second process happens, carbon needs another two photons in order to be ionized and detect the carbon ion. The more photons a process need, the more unlikely it is to occur. Consequently, the green channel is the more likely out of these two.

In the second one,  $CH_2Br^+$  dissociates into methylene radical and ionized bromine with the help of one photon  $(D_0(CH_2 - Br^+)=6.98 \text{ eV})$ . This is the reason why  $CH_2Br^+$ has internal energy which is shown in Eq. 3.12 in order to have positive available energy. Since the methylene radical is neutral, it needs another two photons in order to be ionized and detected. Therefore, the green channel is more likely to occur for the detection of  $CH_2^+$ . However, in terms of bromine ion detection, the red channel has a higher probability of occurrence. Following this dissociation, one photon breaks the bond of methylene radical into methylidyne radical and hydrogen  $(D_0(CH - H)=4.38 \text{ eV})$ , both being neutrals. Just like all the other radicals, CH needs two photons in order to be ionized. The last step in the red channel is the dissociation of CH into C and H  $(D_0(C - H)=3.47 \text{ eV})$ , where we also need two photon to be absorbed by C in order to detect its ion. Overall, the last two steps are much more unlikely to occur compared to the last two steps of the green channel.



Figure 3.12: Energy Diagram of the processes in  $CH_2Br_2$ 

## **Chapter 4**

# Photodissociation of CHBr<sub>3</sub> at 193 nm

### 4.1 Introduction

CHBr<sub>3</sub> is the chemical formula for tribromomethane, most commonly known as bromoform. It was first discovered by French chemist Antoine-Jérôme Balard in 1831. It has a tetrahedral molecular geometry with  $C_{3\nu}$  symmetry. Its molecular weight is 252.73 g/mol. In Figure 4.1, we can see bromoform in 2D and 3D representations.



Figure 4.1: Bromoform in a) 2D and in b) 3D representations

Bromoform is a brominated organic solvent, which can be found in nature in the oceanographic and biogeochemical regime of the subtropical North East Atlantic<sup>14</sup>. It is also produced naturally by algae and kelp<sup>14</sup>. Besides that, it can be produced by synthesis. CHBr<sub>3</sub> is a light yellow liquid at standard temperature and pressure, while also having a sweet smell like CHCl<sub>3</sub>. In earlier times, it served as a solvent for dissolving substances, a sedative for inducing sleep and a flame retardant for preventing fires. However, its current use is mostly restricted to laboratory settings, where it acts as a reagent for different purposes, serving as an extraction solvent. Its density is 2.9 g/cm<sup>324</sup> and the hybridization of the carbon atom is sp<sup>3</sup>. Like dibromomethane, bromoform has been a research topic in the field of photochemistry.

McGivern *et al.*<sup>25</sup> report the photodissociation of CHBr<sub>3</sub> at 193 nm by means of photofragment translational spectroscopy with VUV ionization detection. They identified the primary photodissociation as that between the C and the Br atoms with a second step in the dissociation occurring involving another Br atom.

Xu *et al.*<sup>26</sup> investigated the photolysis of CHBr<sub>3</sub> at 234 and 267 nm with the help of VMI and TOF-MS. They found a 2.3 branchng ratio for  $Br(^{2}P_{3/2})$ : $Br(^{2}P_{1/2})$  products at 267 nm. Besides that, the Br<sub>2</sub> channel had a 0.26 branching ratio at 234 nm and 0.16 at 267 nm, while the atomic Br elimination channel had a 0.76 branching ratio and 0.84 respectively.

Huang et al.<sup>27</sup> studied the photolysis of  $CHBr_3^+$ , produced via VUV laser ionization at 118 nm, by means of TOF-MS and VMI. At 308 nm, they observed  $CBr^+$ ,  $CHBr^+$  and  $CHBr_2^+$  fragments, whereas at 355 and 610 nm they observed  $CHBr_2^+$  only.

CHBr<sup>+</sup><sub>2</sub> fragments, whereas at 355 and 610 nm they observed CHBr<sup>+</sup><sub>2</sub> only.
Zou *et al.*<sup>28</sup> investigated the photodissociation of bromoform at 248 nm, where they observed not only the primary atomic Br loss, but also CHBr. CBr, HBr, Br<sub>2</sub> due to the second step photodissociation of CHBr<sub>2</sub> and CHBr.

Petro *et al.*<sup>29</sup> published a study in which they present a novel observation of a reaction product, that is  $C_2$  with the 2-photon photodissociation of bromoform at 193 nm. Their explanation behind the discovery is that  $C_2$  can be formed by the collision of two electronically excited CH( $A^2\Delta$ ) radicals.

Yang *et al.*<sup>22</sup> reported the multiphoton dissociation of CHBr<sub>3</sub>. The first photon dissociation eliminates atomic Br, the second one eliminates another atomic Br while also electronically exciting the CHBr radical in the  $\tilde{\alpha}^3 A$ " state, and the final photon dissociation produces the electronically excited CH(A<sup>2</sup> $\Delta$ ) and the loss of the third atomic Br.

Haflijason *et al.*<sup>30</sup> obtained the REMPI spectra of CHBr<sub>3</sub> and were examined for twophoton resonant transitions to Rydberg states in the range of 76.000–84.000 cm<sup>-1</sup>. C<sup>+</sup>, CH<sup>+</sup> and <sup>79,81</sup>Br<sup>+</sup> ion fragments were detected. They recorded the REMPI spectrum of CH<sup>+</sup>, while also identifying the different electronic states.

## 4.2 The experiment

I have discussed the experiment in section 3.2 in detail. Readers can refer to that section for a comprehensive understanding of the setup. The ions that we recorded were  $C^+$ ,  $CH^+$ ,  $Br^+$ ,  $CBr^+$  and  $CHBr_2^+$ .

## 4.3 Results

## 4.3.1 Photofragment & Photoelectron Images

In the next figure, we can see the fragment images of the ions that we recorded.



Figure 4.2: The recorded ions

We also recorded CHBr and H, but due to low signal to noise ratio, are not shown here. As mentioned in the previous chapter,  $C^+$  has a perpendicular transition and  $CH^+$  a parallel one. An image of the photoelectrons is presented next.



Figure 4.3: Photoelectrons of CHBr<sub>3</sub>

Just like in the case of the dibromomethane, the photoelectrons of bromoform have zero kinetic energy. However, not all of the photoelectrons of bromoform have zero kinetic energy, in fact, some have the energy that they would have after the ionization of a given fragment. No rings are formed due to the fact that the electrons after the ionization are not plenty. As a result, they are scattered. Some electrons have zero kinetic energy but the energy is distributed among electrons and ions because the latter are in different vibrational states.



Internuclear Distance

Figure 4.4: Potential Energy Surfaces of bromoform

### 4.3.2 The KER distributions

#### $\mathbf{CHBr}_2^+$

The first ion that will be presented will be  $CHBr_2^+$ .



Figure 4.5: CHBr<sub>2</sub><sup>+</sup>

The process that describes the KER of  $CHBr_2^+$  is the one where the parent molecule is ionized and breaks immediately, just like in  $CH_2Br_2$ . The only vibrational modes are those of  $CHBr_2^+$ . In this process, we have a variation of vibrational modes. Due to the molecular beam, parent molecule is in its ground vibrational state.

The case of dissociation of the parent molecule into two neutral fragments, CHBr<sub>2</sub> and Br was examined. This process requires one photon, since  $D_0(CHBr_2 - Br)=2.67 \text{ eV}$ . The energy distributed to the fragments is found from Eq. 1.8 (E(CHBr<sub>2</sub>)=1.18 eV, E(Br)=2.56 eV). As a result, due to the high kinetic energy of the CHBr<sub>2</sub> radical, it would need to have an internal energy of about 3.3 eV, which has a small possibility of happening. Moreover, both CHBr<sub>2</sub> and Br would need to absorb two extra photons in order to be ionized. Overall, three photons would be required in order to detect the ion, which is more unlikely to happen than the process mentioned above with the two photons.

The process that happens is shown in the equations below.

1) CHBr<sub>3</sub> + 2hv 
$$\longrightarrow$$
 CHBr<sub>2</sub><sup>+</sup>( $v_5 = 7 - 9$ ) + Br<sup>\*</sup> + e<sup>-</sup> (4.1)

2) CHBr<sub>3</sub>+2hv 
$$\longrightarrow$$
 CHBr<sub>2</sub><sup>+</sup>( $v_5 = 5, v_6 = 7 - 9$ ) + Br<sup>\*</sup> + e<sup>-</sup> (4.2)

3) CHBr<sub>3</sub> + 2hv 
$$\longrightarrow$$
 CHBr<sub>2</sub><sup>+</sup>( $v_5 = 6, v_6 = 6 - 8$ ) + Br + e<sup>-</sup> (4.3)

where

- $v_5 \rightarrow \text{H deform.} (1229 \text{ cm}^{-1})$
- $v_6 \rightarrow \text{CBr}$  str. (897 cm<sup>-1</sup>)

<u>CBr</u><sup>+</sup>



Figure 4.6: CBr<sup>+</sup>

Following the previous process,  $CHBr_2^+$  dissociates into  $CHBr^+$  and  $Br (D_0(CHBr^+ - Br)=3.65 \text{ eV})$  or CHBr and  $Br^+ (D_0(CHBr - Br^+)=6.55 \text{ eV})$ . One photon is required for both processes, since in the second one the difference between the energy of the photon and the bond dissociation energy is ~0.1 eV, from which we can safely assume that the parent molecule is in a vibrationally excited state.

Thus,  $CHBr^+$  can dissociate into  $CBr^+$  and H. The bond dissociation energy is 4.94 eV. The result of the second process is that CHBr dissociates into CBr and H, with the bond dissociation energy being 3.43 eV. For the reasons mentioned in the previous ion, the first of these two processes is the most probable. The first one is the dissociation of  $CHBr^+$  into  $CBr^+$  and H, where the second one is the dissociation of CHBr into the respective neutral fragments. In the second case, the red vertical lines are those in which CBr is in a vibrationally excited state, whereas in the green vertical lines the reactant is in a vibrationally excited state.

4) 
$$\operatorname{CHBr}^+ + 1\operatorname{hv} \longrightarrow \operatorname{CBr}^+(v_1 = 0 - 11) + \mathrm{H}$$
 (4.4)

5) CHBr + 1hv 
$$\longrightarrow$$
 CBr( $v_1 = 0 - 12$ ) + H (4.5)

6) 
$$\operatorname{CHBr}(v_1 = 1, 2) + 1 \operatorname{hv} \longrightarrow \operatorname{CBr}(X, v = 0) + H$$
 (4.6)

- For  $CBr^+$  :  $v_1$  ( $CBr^+$  str., 1018 cm^{-1})
- For CBr :  $v_1$  (CBr str, 726 cm<sup>-1</sup>)
- For CHBr :  $v_1$  (CH str., 3100 cm<sup>-1</sup>)

#### <u>Br</u><sup>+</sup>

The KER distribution of  $Br^+$  is shown in the next figure. Bromine can be produced by the dissociation of CHBr<sub>2</sub>, CHBr, CBr<sub>2</sub> or CBr, neutrals or ions. Only the first two radicals can produce  $Br/Br^+$ , since CBr<sub>2</sub> ion was not detected, which means that CBr was produced by CHBr, as mentioned in the previous section. Since CBr was detected, we would assume that we could detect Br from this radical. However, the energies distributed among the fragments are larger than the values shown in the KER distributions (E(C)=2.61 eV, E(Br)=0.4 eV). Thus, the only radicals that can produce Br are the first two.



Figure 4.7: Br<sup>+</sup>

Plentiful processes happen, namely eight. These are:

1-3) CHBr<sub>3</sub> + 2hv 
$$\longrightarrow$$
 CHBr<sub>2</sub><sup>+</sup>(Different rovibrational states) + Br/Br<sup>\*</sup> + e<sup>-</sup> (4.7)

7) 
$$\operatorname{CHBr}^+ + 1\operatorname{hv} \longrightarrow \operatorname{CH}^+(A, v_2 = 2 - 4) + \operatorname{Br}$$
 (4.8)

8) 
$$\operatorname{CHBr}^+(v_2 = 0 - 3) + 1 \operatorname{hv} \longrightarrow \operatorname{CH} + \operatorname{Br}^+$$
 (4.9)

9) CHBr + 1hv 
$$\longrightarrow$$
 CH( $v_1 = 5 - 7$ ) + Br\* (4.10)

10) 
$$\operatorname{CHBr}_{2}^{+}(v_{5} = 1, 2) + 1 \operatorname{hv} \longrightarrow \operatorname{CHBr} + \operatorname{Br}^{+}$$
 (4.11)

11) 
$$\operatorname{CHBr}_{2}^{+} + 1 \operatorname{hv} \longrightarrow \operatorname{CHBr}^{+}(v_{1} = 6, v_{2} = 1) + \operatorname{Br}$$
 (4.12)

with the vibrations being

- For  $\text{CHBr}_2^+$ :  $v_5$  (H deform., 1229 cm<sup>-1</sup>),  $v_6$  (CBr str. (897 cm<sup>-1</sup>))
- For CHBr<sup>+</sup> :  $v_1$  (CH str., 3192 cm<sup>-1</sup>),  $v_2$  (CBr str. 983 cm<sup>-1</sup>)
- For CH :  $v_1$  (X<sup>2</sup> $\Pi_2$ , 2858.5 cm<sup>-1</sup>)
- For CH<sup>+</sup> :  $v_2$  ( $A^1\Pi$ , 1848 cm<sup>-1</sup>)

It is obvious that two processes produce neutral Br and the other two produce  $Br^+$ . In the first case, the other fragment is in a vibrationally excited state, whereas in the reactant is in a vibrationally excited state.

#### $\underline{CH^+}$

CH<sup>+</sup> can be produced by the photodissociation of CHBr<sup>+</sup> or of CHBr. In the first process, two things can occur. Firstly, CHBr<sup>+</sup> can dissociate into CH<sup>+</sup> and Br, which will result in  $E(CH^+)= 1.14 \text{ eV}$  and  $E(Br) \sim 0.19 \text{ eV}$ . If Br is in its excited state  ${}^2P_{1/2}$  and CH<sup>+</sup> has  $\sim 0.7 \text{ eV}$  in internal energy, then we get values that can be depicted in both KER distributions. The same process can be followed if bromine is in its ground state. We can follow this procedure for the case where bromine is the one getting ionized and methylene remains neutral. In the second process, CHBr absorbs one photon and dissociates into CH and Br, with E(CH)=2.62 eV and E(Br)=0.43 eV. As a result, CH would have to be in a vibrationally high state, i.e. have  $\sim 2.5 \text{ eV}$  in internal energy. This scenario is more unlikely than the first one due to the high internal energy of the methylene and the number of photons needed for its ionization.

Since bromoform has three bromine, one carbon and one hydrogen atoms, we can safely assume that these are the only processes that occur.



Figure 4.8: CH<sup>+</sup>

7) 
$$\operatorname{CHBr}^+ + 1\operatorname{hv} \longrightarrow \operatorname{CH}^+(A, v_1 = 2 - 4) + \operatorname{Br}$$
 (4.13)

8) 
$$\operatorname{CHBr}^+(v_2 = 0 - 3) + 1 \operatorname{hv} \longrightarrow \operatorname{CH} + \operatorname{Br}^+$$
 (4.14)

9) CHBr + 1hv 
$$\longrightarrow$$
 CH( $v_1 = 5 - 7$ ) + Br\* (4.15)

where

- For CHBr<sup>+</sup> :  $v_1$  (CH str., 3192 cm<sup>-1</sup>),  $v_2$  (CBr str. 983 cm<sup>-1</sup>)
- For CH :  $v_1$  (X<sup>2</sup> $\Pi_2$ , 2858.5 cm<sup>-1</sup>)
- For CH<sup>+</sup> :  $v_1 (A^1\Pi, 1848 \text{ cm}^{-1})$

 $\underline{\mathbf{C}^+}$ 

We have the three possible reactions that can take place if the reactants are CH<sup>+</sup> and CH. Process 4.17 explains roughly one third of the spectrum, with the other two thirds being described by the other two processes. An interesting part of the graph is the peak shown from 0 to  $\sim 0.05$  eV, which is probably due to the formation of carbon clusters. Clusters, being much heavier than atoms, have lower kinetic energy due to conservation of momentum.



Figure 4.9: C<sup>+</sup>

Carbon can be also be produced from the photodissociation of CBr<sup>+</sup>. It is not included in the processes that can occur since if CBr<sup>+</sup> dissociates into  $C^+$  (E(C<sup>+</sup>)=1.89 eV) and Br (E(Br)=0.29 eV), then the values are too high for the KER distributions. This means that the ions from this process are not projected onto the position sensitive detector. This also applies in the case where bromine receives the positive charge (E(Br<sup>+</sup>)=0.21 eV) and carbon remains neutral (E(C)=1.41 eV).

As stated, three processes occur in this graph. These are

12) 
$$CH^+(v_1 = 0 - 6) + 1hv \longrightarrow C^+ + H$$
 (4.16)

13) 
$$\operatorname{CH}^+(v_1 = 0 - 6) + 1 \operatorname{hv} \longrightarrow \operatorname{C} + \operatorname{H}^+$$
 (4.17)

14) 
$$CH(v_1 = 0 - 4) + 1hv \longrightarrow C + H$$
 (4.18)

where

- For CH<sup>+</sup> :  $v_1 (X^1 \Sigma^+, 2858 \text{ cm}^{-1})$
- For CH :  $v_1$  (X<sup>2</sup> $\Pi_2$ , 2858.5 cm<sup>-1</sup>)

We have the three possible reactions that can take place if the reactants are  $CH^+$  and CH. Process 4.17 explains roughly one third of the spectrum, with the other two

thirds being described by the other two processes. An interesting part of the graph is the peak shown from 0 to  $\sim 0.05$  eV, which is probably due to the formation of carbon clusters. Clusters, being much heavier than atoms, have lower kinetic energy due to the conservation of momentum.

Carbon can be also be produced from the photodissociation of CBr<sup>+</sup>. It is not included in the processes that can occur since if CBr<sup>+</sup> dissociates into  $C^+$  (E(C<sup>+</sup>)=1.89 eV) and Br (E(Br)=0.29 eV), then the values are too high for the KER distributions. This means that the ions from this process are not projected onto the position sensitive detector. This also applies in the case where bromine receives the positive charge (E(Br<sup>+</sup>)=0.21 eV) and carbon remains neutral (E(C)=1.41 eV).

### 4.3.3 Discussion

Just like in the previous discussion, section 3.3.3, I will present the most probable channels that happen in the photodissociation of CHBr<sub>3</sub> below.



Figure 4.10: The processes of CHBr<sub>3</sub>'s photodissociation

In contrast to the three channels of dibromomethane, tribromomethane has six channels, although the first step is same in both molecules. The neutral parent molecule is ionized and dissociates into  $\text{CHBr}_2^+$ , Br and e<sup>-</sup>. One photon is not enough for this process, since one photon of 193 nm is equal to 6.42 eV, the ionization energy is 10.5 eV and the bond dissociation energy  $D_0(\text{CHBr}_2^+ - \text{Br})=0.49$  eV. Thus, two photons are needed in order to have processes 4.7-4.3. The available energy is 1.85 eV if we have Br (E(CHBr\_2^+)=0.59 eV, E(Br)=1.27 eV) and 1.39 eV if we have Br\* (E(CHBr\_2^+)=0.44 eV, E(Br\*)=0.95 eV). We reach the conclusion that the products, namely CHBr\_2^+, must have internal energy in order to get the KER values observed, which are seen in the processes 4.7-4.3. Furthermore, more than one vibrations may be present in this product in said processes.

The first channel that will be discussed is the green one. In this channel,  $CHBr_2^+$  dissociates into  $CHBr^+$  and  $Br/Br^*$  ( $D_0(CHBr^+ - Br)=3.65 \text{ eV}$ ). Since we did not take any images of  $CHBr^+$ , we have to take into consideration only the bromine fragment, as to the fact if this process can occur. The fact that there are no images of  $CHBr^+$  does

not mean that there wasn't any produced in the chamber after the interaction of the two beams, but simply means that it was in such a small quantity which made it difficult to detect when we were adjusting the time delay between the two beams, or that we missed it since the difference between  $CBr^+$  and  $CHBr^+$  is very small. In order to have KER values that fit the spectrum of  $Br^+$ , Figure 4.7,  $CHBr^+$  must have internal energy. This process is 4.12. Following this step,  $CHBr^+$  absorbs another photon that leads into three different channels. All of these three channels are possible, since there are ions that we detected.

The green channel is the one where CHBr<sup>+</sup> dissociates into CH<sup>+</sup> and Br ( $D_0(CH^+ - Br)=5.09 \text{ eV}$ ). This process is shown in eq. 4.13, in which CH<sup>+</sup> must have the internal energy shown in this process. It is shown in both the spectrum of Br<sup>+</sup> and CH<sup>+</sup>, although since the bromine is neutral, it needs another two photons to be ionized. The final step of this channel is the one in which the bond of CH<sup>+</sup> breaks into C<sup>+</sup> + H ( $D_0(C^+ - H)=4.13$  eV) and/or C + H<sup>+</sup> ( $D_0(C - H^+)=6.47$  eV). The first process (eq. 4.16) is much more likely to occur, since C has the positive charge. Due to the fact that  $D_0(C^+ - H)=4.13$  eV, the energy of bromine is ~0.175 eV without any internal energy of CH<sup>+</sup>, while if CH<sup>+</sup> has the vibrations shown in this process, it can explain the graph from this point until the end.

Moreover, CHBr<sup>+</sup> can break into CBr<sup>+</sup> and H ( $D_0(CBr^+ - H)=4.94 \text{ eV}$ ), process 4.4. It explains one third of the graph 4.6, with the first value being the one which does not have any internal energy, while the other KER values are those in which CBr<sup>+</sup> is in its stretching vibrational mode. CBr<sup>+</sup> may dissociate into C + Br<sup>+</sup> or C<sup>+</sup> + Br, but the energies after the dissociation are pretty large, E(C)=1.42 eV, E(Br<sup>+</sup>)=0.22 eV and E(C<sup>+</sup>)=1.89 eV, E(Br)=0.29 eV, respectively.

The other process that can occur is that the  $CH - Br^+$  bond can break. This process is shown in eq. 4.14. The energy that is distributed to the CH radical is 0.13 eV, while the energy that is distributed to  $Br^+$  is 0.02 eV. As a result, we can assume that  $CHBr^+$  is in the vibrationally excited state CBr str. (0.12 eV), as can be seen in the orange vertical lines in Figure 4.7. The corresponding energies of CH are shown in also in the orange vertical lines in Figure 4.8. The final step of this channel is C and H, which can take place after one photon is absorbed by CH (process 4.18). This process describes some of the second part of the diagram (Figure 4.9). After the photolysis with one photon, the available energy of CH is 2.91 eV, thus the energy that is attributed to carbon is ~0.23 eV, while that of hydrogen is ~2.69 eV, which is the difference of the other two. This is the reason why we can speculate that CH is in its stretching vibrational mode, in order to cover more part of the graph instead of having only the one value of the ground state. This reaction has a smaller chance of occurrence in relation to the other processes, C<sup>+</sup>+H and C+H<sup>+</sup>, as we need another two photons to ionize C or H.

Instead of the green channel, where Br is neutral and CHBr receives the positive charge, the inverse reaction can happen, i.e. Br receives the positive charge and CHBr remains neutral. This is the red channel. Equation 4.11 describes this process for the bromine graph, since we do not have any image for CHBr, as mentioned before. The process can occur with one photon, only if  $CHBr_2^+$  is in a vibrationally excited state (H deform., 0.15 eV), which will add the necessary internal energy to have positive available energy. In the case which  $CHBr_2^+$  is in its ground state (X,v=0), the process would need two photons to occur. CHBr is separated in two branches. I will start with the one in red, and discuss the blue one later on.

As soon as one photon interacts with CHBr, the bond between CH and Br can break

 $(D_0(CH^+ - Br)=3.37 \text{ eV})$ , which will result in the respective neutrals (4.15). One photon is enough to provide CHBr with 3.05 eV. As a result, we can hypothesize that Br is in its excited state, Br\*, which will result in a smaller number of modes of CH ( $X^2\Pi_r$ , 0.35 eV). Since the fragments that we get from this process are neutral, the likelihood of it occurring is smaller than the three branches from the green channel, as both CH (Ionization Energy=10.64 eV) and Br need two photons to be ionized. CH can then absorb one photon and break into C and H fragments, which was discussed previously.



Figure 4.11: Energy diagram of CHBr<sub>3</sub>

The other branch is the one where CHBr breaks into CBr and H ( $D_0(CBr - H)=3.43$  eV). The available energy that is attributed to CHBr will be 2.99 eV, with CBr receiving 0.032 eV. As a result, we can speculate that CBr is in its stretching vibrational mode (0.09 eV). The values that we get are shown in the red vertical lines in Figure 4.6 from equation 4.5.

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