Slice Imaging Studies of the Ultraviolet Photodissociation of Dihalogens and Halomethanes

Andreas Kartakoullis

Department of Chemistry, University of Crete and Institute of Electronic Structure and Laser,

Foundation for Research and Technology - Hellas



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PhD Committee

- 1. Dr. Theofanis Kitsopoulos (Supervisor), Professor, University of Crete
- 2. Dr. Stavros Farantos, Professor, University of Crete
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- 7. Dr. Michalis Velegrakis, Research Director, Foundation for Research and Technology Hellas

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Abstract

Understanding photochemistry at the molecular level in the bulk requires an answer to the question: *How does photodissociation change with solvation from the individual molecule to the corresponding bulk?* Photodissociation studies in clusters are a viable approach to tackle this problem. In this respect, clustering of molecules with xenon atoms can provide a valuable insight: Xe as the rare gas atom serves as an archetype of chemically non-reactive solvent, yet its interaction can be strong enough to cause electronic effects. In addition, due to its high mass it tends to cluster easily with molecules in supersonic expansions.

In Chapter 5 we will present the results of iodine monochloride (ICl) photolysis in the ultraviolet region of the spectrum (235-265 nm) studied with the use of Slice Imaging technique. We find that ground state chlorine atoms $Cl({}^{2}P_{3/2})$ are formed nearly exclusively with excited state iodine atoms $I({}^{2}P_{1/2})$, while excited spin-orbit chlorine atoms $Cl({}^{2}P_{1/2})$ are concurrently produced only with ground state iodine atoms $I({}^{2}P_{3/2})$. We conclude that photolysis of ICl in this UV region is a relatively "clean" source of spin-orbit excited chlorine atoms that can be used in crossed molecular beam experiments.

In Chapter 6, slice imaging data are demonstrating the influence of clustering on the photodissociation dynamics of a diatomic molecule: following the results of Chapter 5, ICl was dissociated at 235 nm in He and Xe seed gasses, probing both Cl and I photofragment energy and angular distributions. We observe that the kinetic energy releases of both Cl and I fragments change from He to Xe seeding. For Cl fragments, the seeding in Xe increases the kinetic energy release of some Cl fragments with a narrow kinetic energy distribution, and leads to some fragments with rather broad statistical distribution falling off exponentially from near-zero energies up to about 2.5 eV. Iodine fragment distribution changes even more dramatically from He to Xe seeding: sharp features essentially disappear and a broad distribution arises reaching to about 2.5 eV. Both these observations are rationalized by a simple qualitative cluster model assuming ICl dissociation inside larger xenon clusters and "on surface" of smaller Xe species.

Finally, Chapter 7 introduces the state resolved dynamics of CH_3I when clustered in a supersonic expansion using He and Xe as seeding gases. Following excitation at 193 nm (6.4 eV), state specific alterations in photodissociation dynamics are observed. Four vibrational levels ($\nu_2 = 0, 1, 2, 3$) of the CH_3 umbrella vibrational mode were probed, as were $I({}^2P_{3/2})$ and $I({}^2P_{1/2})$ atomic photofragments. For nascent CH_3 fragments the measured kinetic energy releases and angular distributions show enormous sensitivity to the clustering. Manifestation of the clustering dynamics include: (a) shifting to higher energies (by up to 0.5 eV) and significant broadening of the kinetic energy distribution; (b) vibrational dependence of this increase in product kinetic energy; (c) angular distribution changes from a characteristic perpendicular character observed in free-standing CH_3I into a parallel transition for the clustered moiety. Drastic effects of clustering are also observed when probing iodine-atom photofragments, namely the state resolved distribution observed when seeding in He is replaced by a broad structureless distribution when seeding in Xe.

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Chapter 1 Introduction

The breaking and formation of chemical bonds is the alpha and the omega in Chemistry. Research in *Molecular Reaction Dynamics* aims to give a full understanding of the mechanisms behind these processes, which are essential to determine the function and the evolution of chemical and biological systems. Levine and Bernstein [2] in their classic textbook have stated that Molecular Reaction Dynamics is the study of elementary chemical processes and the means of probing them, understanding them, and controlling them with the last one being the ultimate goal. It can be applied to reactions in solutions (liquid phase), on surfaces (condensed phase) and in gases (gas phase). The main subject of the thesis is the study of clustering effects, which is considered as the bridge between gas phase and condensed phase

1-1 Imaging Molecular Dynamics

Imaging Molecular Dynamics was introduced due to the Chandler and Houston pioneering work with the invention of Ion Imaging in their 1987 seminal paper [3]. The first imaging experiment was on the state-selective photodissociation of methyl iodide (CH₃I), where the three-dimensional velocity distribution of the nascent photofragments was projected on a micro-channel plate (MCP) detector coupled to a phosphor screen and visualised with the use of inverse Abel transform as a two-dimensional image. It was shown for the first time, that angular and speed distribution from molecular photodissociation could be measured simultaneously.

Currently the field has evolved significantly with the advent of other charged particle imaging methods such as Velocity Map Imaging (VMI) and Slice Imaging [4–7]. VMI was introduced by Eppink and Parker [8] and improved significantly the energy resolution by almost an order of magnitude to 2% - 5%. An electrostatic

lens was placed in the acceleration region that focuses ions with similar velocities at a common point on the imaging plane thus Velocity Map Imaging. However, the inverse Abel transform has the necessity for cylindrical symmetry parallel to the imaging plane and so sets a restrain on the kind of experiments that VMI can be applied to. Kitsopoulos and coworkers in 2001 introduced *Slice Imaging* where the inverse Abel transform is no longer needed [1]. This is achieved by using delayed pulsed extraction of the ions and handling the resulting ion cloud size over the time-of-flight (TOF) axis. Subsequently, a narrow electrical detector-gating pulse can extract and image the center slice of the ion cloud directly from the three-dimensional spatial photofragment distribution. Slice imaging allows for non-cylindrically symmetric distributions to be imaged and analyzed with ease, thus improving the sensitivity of the imaging method towards spatial anisotropy parameter measurements.

1-2 Photodissociation in molecular dynamics studies

Some processes of interest in gas-phase studies are simple two-body events and they can be categorised in two types of elementary reactions:

- 1. Unimolecular Reaction where a molecule AB can be excited to (AB)* state by absorption of one or more photons and break into two fragments A and B (e.g. Molecular Photodissociation)
- 2. Bimolecular Reaction where a collision/reaction between two molecules AB and C takes place (e.g. Reactive Scattering)

Their complete understanding requires detailed knowledge of the Potential Energy Surfaces (PES) for the process and the dynamics of motion on that surface. By controlling the experimental molecular properties of the parent molecule such as laboratory velocity, internal temperature, axis or rotational angular momentum alignment, and then characterising the final products afterwards, one could easily understand the *before* and the *after* of the process. Let's consider a photodissociation event that yields two fragments flying with equal momentum in opposite directions in the centre-of-mass frame. Repeating the same event many times, the fragments build up spherical distributions in lab-frame. Therefore, we could use *Newton spheres* for representing the process, where the size correlates directly to the translational energy and the surface pattern indicates the directionality of the process.

1-2.1 Dihalogens: Iodine Monochloride (ICl)

Heteroatomic dihalogens such as ICl, BrCl, and IBr have a rich photochemistry that exhibits many curve crossings and avoided crossings in the excited potential curves. For that reason their photodissociation dynamics have attracted significant theoretical and experimental attention. Furthermore, they are premium photolytic sources to be used for studying reactivity between ground and spin-orbit excited states for a given.

Iodine Monochloride (ICl) literature is not as extended as that of the other dihalogens. The molecule exhibits very interesting photochemistry with two broad bands peaking at 270 nm and 470 nm, respectively. The former band is the main focus of this thesis and has the following dissociation process allowed:

- (1) $ICl(v=0) + h\nu \rightarrow I({}^{2}P_{3/2}) + Cl({}^{2}P_{3/2}) \qquad \Delta E = 2.15 \text{eV},$
- (2) ICl(v=0) + h $\nu \rightarrow I({}^{2}P_{3/2}) + Cl^{*}({}^{2}P_{1/2}) \qquad \Delta E = 2.26 \text{eV},$
- (3) $ICl(v=0) + h\nu \rightarrow I^*({}^2P_{1/2}) + Cl({}^2P_{3/2}) \qquad \Delta E = 3.09 \text{eV},$
- (4) ICl($\nu = 0$) + h $\nu \rightarrow I^*({}^2P_{1/2}) + Cl^*({}^2P_{1/2}) \qquad \Delta E = 3.20 \text{eV}$

Channel (4) is not active in our region of interest that covers the ultraviolet part of the spectrum (235nm - 265nm). We have carefully selected three distinct wavelengths at 235 nm, 250 nm and 265 nm covering the higher energy part of the absorption band. Our results have shown an almost exclusive production of Cl^* with ground state Iodine atoms, while the opposite is true for Cl, i.e. the concomitant production of I^{*}. This makes ICl a suitable precursor molecule for photolytic studies of the relative reactivity of Cl and Cl^{*}.

1-2.2 Halomethanes: Methyl Iodide (CH_3I)

The plethora of studies on the photodissociation of CH_3I , especially in its first absorption band (A-band), have constituted CH_3I as a prototypical molecule for studying dissociation processes in polyatomic molecules. The diatomic-like breaking of the C - I bond combines the simplicity of unidimensional bond breaking with the complexity of polyatomic molecular dynamics, such as different absorbing states, nonadiabatic crossings, and energy partitioning between electronic, vibrational, and rotational states.

1-3 Organisation and Scope of the Thesis

The main aim of this thesis is to give an insight of clustering effects on the reactivity of halomethanes and dihalogens such as methyl iodide and iodine monochloride. In Chapter 2 fundamental principles of quantum mechanics for diatomic molecules and spectroscopic transitions are described. In Chapter 3, the processes involved in gas-phase dynamics and how they can be interpreted by exploiting ion imaging are discussed. In Chapter 4 a comprehensive description on the formation of pulsed molecular beams, gas dynamics, free-jet expansion and cluster formation is given. Chapter 5 the results obtained from the ultraviolet photodissociation of ICl at 235, 250, and 265 nm will be presented and discussed. In Chapter 6 the first clustering study of ICl with Xe will be presented and discussed. In Chapter 7 we will present the second clustering study of methyl iodine with Xe and we will discuss the different dynamics for the two absorption bands involved.

Chapter 2

Molecular Reaction Dynamics

The main research interest of the thesis is gas-phase molecular reaction dynamics where most of the processes are simple two-body events that can be classified either as unimolecular (or half-collision event) or as bimolecular (or full-collision) reactions. The molecules studied in the thesis are diatomic (ICl) or pseudo-diatomic molecules (CH_3I), thus a review of diatomic molecule quantum mechanics and of the mechanisms of ultraviolet photodissociation will be given in this chapter.

The evolution of a diatomic molecule in time and space can be described by the time-independent Schrödinger equation:

$$\hat{H}\Psi = i\hbar\frac{\partial}{\partial t}\Psi \tag{2.1}$$

and the Hamiltonian operator can be expanded as:

$$\hat{H} = \hat{T}_N + \hat{T}_e + V_{NN} + V_{ee} + V_{Ne}$$
(2.2)

where \hat{T}_N is the kinetic energy of the nuclei, \hat{T}_e is the kinetic energy of the electrons, V_{NN} is the repulsive electrostatic potential energy of the nuclei, V_{ee} is the repulsive electrostatic potential energy of the electrons, and V_{Ne} is the attractive electrostatic potential energy between the nuclei and electrons.

The time-independent Schrödinger equation can not be analytically solved but only with the use of different approximations such as the *Born-Oppenheimer* approximation, according to which electrons move so much faster than the nuclei that their motion can be separated. Thus the wave function Ψ can be expressed as the product of an electronic wave function Ψ_e and a nuclear wave function Ψ_N :

$$\Psi = \Psi_e(\mathbf{R}, \mathbf{r})\Psi_N(\mathbf{R}) \tag{2.3}$$

where Ψ_e depends on both the nuclear coordinates **R** and electronic coordinates **r**, while Ψ_N only depends on the **R** coordinates. The electronic wave function Ψ_e is a solution to the electronic Schrödinger equation, which describes the motion of the electrons and the electronic energy E_e :

$$(\hat{T}_N + \hat{T}_e + V_{ee} + V_{Ne})\Psi_e(\mathbf{R}, \mathbf{r}) = E_e(\mathbf{R})\Psi_e(\mathbf{R}, \mathbf{r})$$
(2.4)

The wave function $\Psi_N(\mathbf{R})$ is the solution to the nuclear Schrödinger equation:

$$(\hat{T}_N + V_{NN} + E_e(\mathbf{R}))\Psi_N(\mathbf{R}) = E\Psi_N(\mathbf{R})$$
(2.5)

where the sum of $V_{NN} + E_e(\mathbf{R})$ represents the potential energy $V(\mathbf{R})$ of nuclei as a function of their position, which is known as the *Potential Energy Surface* (PES). Inserting $V(\mathbf{R})$ into Eq. 2.5 gives:

$$(\hat{T}_N + V(\mathbf{R}))\Psi_N(\mathbf{R}) = E\Psi_N(\mathbf{R})$$
(2.6)

where the term $\hat{T}_N + V(\mathbf{R})$ is the quantum Hamiltonian operator for the translational, vibrational, and rotational motion of the molecule.

2-1 Diatomic Molecules Quantum Mechanics

2-1.1 Rotation: The Rigid Rotor

Diatomic molecules such as ICl belong to the point group $C_{\infty v}$ and their rotation can be modelled with the use of the rigid rotor, illustrated in Fig. 2.1. Suppose that the two nuclei (m_1, m_2) are fixed at their equilibrium separation r_e ; then the molecule could rotate around the center-of-mass (cm) defined such that $m_1r_1 = m_2r_2$. The classical Hamiltonian of the rigid rotor with angular frequency ω is:

$$\hat{H} = \hat{T} = \frac{1}{2}I\omega^2 = \frac{J^2}{2I}$$
(2.7)

where J is the angular momentum of the rigid rotor and I the moment of inertia defined as:

$$I = \frac{m_1 m_2}{m_1 + m_2} r_e^2 = \mu r_e^2$$

where μ is called the reduced mass of the system. Considering now quantum mechanics, it is well known that the operator J^2 has eigenvalues $J(J+1)\hbar^2$ [9], thus the energy of the rigid rotor for the *J*th rotational level is:

$$E_{J} = \frac{\hbar^{2}}{2I}J(J+1) = \frac{\hbar^{2}}{2\mu r_{e}^{2}}J(J+1)$$

$$E_{J} \equiv \bar{B}J(J+1)$$
(2.8)

where J is the rotational quantum number with integer values J = 0, 1, 2, ... and the rotational constant $\bar{B} = B/hc$ can be expressed in wavenumbers units (cm^{-1}) .

The modelling of the molecule as a rigid rotor is only an approximation. As we move to higher J the bond is getting stretched and a nonrigid rotor model must be consider:

$$E_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2$$
(2.9)

where D is called the centrifugal distortion constant because it is a measure of the increased bond length resulting front he rotation of the molecule.

2-1.2 Vibration: The Harmonic and the Anharmonic Oscillator

The one-dimensional molecular potential energy $V(x + \Delta x)$ of a diatomic molecule increases if the nuclei are displaced from their equilibrium positions. When the dis-



Figure 2.1: The rigid rotor

placement Δx is very small, then the Taylor expansion can be used as follows:

$$V(x + \Delta x) = V(0) + \left. \frac{dV}{dx} \right|_{x=0} \Delta x + \left. \frac{dV^2}{d^2 x} \right|_{x=0} (\Delta x)^2 + \cdots$$

Considering that V(0) = 0, also the first derivative is zero because at equilibrium the potential is at a minimum and higher-order terms of (Δx) can be neglected. The potential becomes:

$$V(x) = \frac{1}{2}kx^2$$
 where $k = \frac{d^2V}{dx^2}\Big|_{x=0}$ (2.10)

which is actually the potential energy of the harmonic oscillator that has force constant k and with the following energy levels:

$$E_{\nu} = (\nu + \frac{1}{2})\hbar\omega \quad where \quad \omega = \sqrt{\frac{k}{m}}$$
(2.11)

with the vibrational quantum number $\nu = 0, 1, 2, \ldots$

The energy levels, that include rotation and vibrational contributions, are:

$$E_{\nu,J} = (\nu + \frac{1}{2})\hbar\omega + \bar{B}J(J+1) - \bar{D}J^2(J+1)^2$$
(2.12)

As with the rigid rotor, we have made an approximation by neglecting the higherorder terms in the Taylor expansion of the molecular potential. In real molecules the neglected terms are important, particularly for large displacements from equilibrium. Furthermore, the confining parabolic form of the harmonic oscillator energy, makes the dissociation impossible. It follows that the Anharmonic Oscillator is more suitable to approximate a diatomic molecule with a *Morse potential*:

$$V(x) = hcD_e \left[1 - exp(-\alpha x)\right]^2$$
(2.13)

where D_e is the minimum and the depth of the Morse potential shown in Fig. 2.2 and α is a measure of the curvature at the bottom of the potential well.

Solving now the Schrödinger equation for this potential we get the following energy levels:

$$E_{\nu} = (\nu + \frac{1}{2})\hbar\omega_e - (\nu + \frac{1}{2})^2\hbar\omega_e x_e$$
(2.14)

where x_e is called the anharmonicity constant. As shown in Fig. 2.2 D_0 is related to



Figure 2.2: The Morse potential

the minimum of the well D_e and to the zero-point energy of the oscillator:

$$D_0 = D_e - \frac{E_0}{hc} = D_e - \frac{1}{2}\omega_e + \frac{1}{4}\omega_e x_e$$
(2.15)

The energy levels of a rotating, vibrating diatomic molecule under the approximation of the anharmonic oscillator are given by:

$$E_{\nu,J} = (\nu + \frac{1}{2})\hbar\omega_e - (\nu + \frac{1}{2})^2\hbar\omega_e x_e + \bar{B}J(J+1) - \bar{D}J^2(J+1)^2 - \alpha_e(\nu + \frac{1}{2})J(J+1) \quad (2.16)$$

The first two terms are giving the vibrational energy levels of the anharmonic oscillator, the second two terms are giving the rotational energy levels and the last term represents the interaction between vibration and rotation which is known as *Rotational-Vibrational Coupling* [9].

2-2 Molecular Electronic Transitions

The energy of a rotational transition is usually less than for vibrational transitions and the energy of vibrational transitions is usually less than for electronic transitions. Therefore, it is possible to observe pure rotational transitions, a vibrational transition is normally accompanied by rotational transitions, and electronic transitions are accompanied by both vibrational and rotational transitions. The complication goes further when considering multiple sources of angular momentum that are coupled together. The coupling of angular momentum enables us to derive term symbols that specify the symmetry of the state, and then to use those term symbols to express the



Figure 2.3: The orbital and spin angular momenta and their projections in Hunds case (a)

selection rules.

2-2.1 Hund's Coupling Cases: Spin-Orbit Coupling

Hund's coupling cases are idealised situations which help us understand the pattern of rotational levels and the resulting spectra, especially the coupling of electronic and rotational motion. Furthermore, they can provide a comprehensive definition of molecular parameters useful for the determination of the transition selection rules.

The three basic sources of angular momentum in a diatomic molecule are: (i) the spin of the electrons \mathbf{S} , (ii) the orbital angular momentum \mathbf{L} , and (iii) the rotation of the nuclear framework \mathbf{R} . They can be coupled by a number of different interactions with the result being the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S} + \mathbf{R}$. The Hund coupling case (a) is depicted in Fig. 2.3, where the orbital angular momentum \mathbf{L} is coupled strongly to the internuclear axis, and the spin is coupled to \mathbf{L} by *spin-orbit* coupling and coupled also to the internuclear axis. Therefore, we have to use their projections on the internuclear axis of the spin \mathbf{S} and the angular momentum \mathbf{L} denoted by Σ and Λ respectively. \mathbf{L} and \mathbf{S} are not quantised and only their projection is consider



Figure 2.4: Components of the total angular momentum \mathbf{J} in the laboratory (X,Y,Z) and molecular (x, y, z) coordinate systems.

as a quantum number:

$$\Lambda = \sum_{i=1}^{N} \lambda_i \tag{2.17}$$

$$S = \sum_{i=1}^{N} s_i \tag{2.18}$$

in which λ_i is the projection of the *i*th electronic orbital angular momentum l_i . The total angular momentum of the molecule **J** has magnitude $\sqrt{J(J+1)}\hbar$, with a component **R** perpendicular to the internuclear axis that rises from the rotation of the nuclear framework. It also has a component Ω parallel to the internuclear axis arising from the electronic angular momentum around the axis, that is related to the components of orbital and spin angular momenta by:

$$\Omega = |\Lambda + \Sigma| \tag{2.19}$$

The total angular momentum **J** as always has a projection M_J into the laboratory frame as illustrated in Fig 2.4. The various angular momenta and their projections onto the molecular axis are summarized in Table 2.1

Hund's case (a) is considered to be the most common for diatomic molecules, however in the case of heavy molecules the coupling between **L** and **S** may be stronger than the interaction with the internuclear axis. An example of Hund's case (c) illustrated in Fig. 2.5 where the spin-orbit coupling is quite strong. In this case their projections Λ and Σ can not be defined, and the spin-orbit coupling gives a resultant **E** with a projection on the axis Ω .

Angular Momentum	Projection on Molecular Axis
J	$\Omega = \Lambda + \Sigma $
\mathbf{L}	Λ
\mathbf{S}	Σ
\mathbf{R}	_

Table 2.1: Angular momenta in diatomic molecules.



Figure 2.5: A vector diagram for Hund's case (c) $\,$

2-2.2 Notation

A diatomic molecule has a molecular axis of cylindrical symmetry, which is the internuclear bond axis, and we have to define new quantum numbers as projections on this molecular axis. We have shown how we can relate Ω to the orbital **L** and spin **S** quantum numbers depending on the type of coupling between the different angular momenta. When the electric field gradients between the nuclei are high, especially at small internuclear separations, **L** and **S** may couple separately to the internuclear axis, making projections Λ and Σ respectively, with total projection Ω , this is referred to as Hund's case (a) coupling. When the electric field gradients are weak, at larger internuclear separation, the spin and orbital angular momenta couple to each other, but the total projection on the internuclear axis Ω , remains a good quantum number, we refer to this coupling scheme as Hund's case (c).

The wavenumber of a transition $\tilde{\nu}$ is defined as the difference between the energies of two terms expressed as wavenumbers:

$$\tilde{\nu} = T' - T \tag{2.20}$$

A transition is denoted $T' \to T$ for emission and $T' \leftarrow T$ for absorption, with the term T' higher in energy than the term T. The notation for atomic or molecular terms can be labeled based on their electronic configuration, i.e. the specification of the orbitals that the electrons occupy. The level of each term arising from a particular configuration is summarized by a *term symbol*:

 $\stackrel{\text{multiplicity} \to 2S+1}{L} \underset{J \leftarrow level}{\longleftarrow} \text{orbital angular momentum for atoms}$

where $\{L\}$ is a letter (S,P,D,F, etc.) corresponding to the total angular momentum quantum number L (0, 1, 2, 3, etc.). The multiplicity of a term is the value of 2S+1, where S is the total electronic spin angular momentum quantum number, and if $L \ge S$ the multiplicity is the number of levels of the term.

In the case of diatomic molecules the notation parallels that for atoms:

$${}^{2\mathbf{S}+1}\{\Lambda\}_{\Omega} \tag{2.21}$$

where Λ is a Greek capital letter ($\Sigma, \Pi, \Delta, \Phi, etc.$) corresponding to Λ (0, 1, 2, 3, etc.), and Ω quantum number is used as a subscript to label a particular spin component. For example, if $\Lambda = 1$, $\Sigma = \pm 1/2$ the result is a ² Π state with 2S + 1 = 2 spin components, ² $\Pi_{3/2}$ and ² $\Pi_{1/2}$. The spin components are labeled by their $|\Omega|$ values



Figure 2.6: The low-lying electronic states of the O_2 molecule. From "Spectra of Atoms and Molecules" by Peter F. Bernath, copyright Oxford University Press, Inc.

except when $S > |\Lambda| > 0$ and $\Omega = |\Lambda| + \Sigma$ is used then. For example, a ⁴ Π state with S = 3/2, $\Lambda = 1$ has spin components labeled as ⁴ $\Pi_{5/2}$, ⁴ $\Pi_{3/2}$, ⁴ $\Pi_{1/2}$ and ⁴ $\Pi_{-1/2}$. An additional labelling for the electronic states of diatomic molecules, is X for ground state, and A, B, C for excited states of the same multiplicity as the ground state, in order of increasing energy. States with a multiplicity different from that of the ground state are labeled with lowercase letters a, b, c, and so on, in order of increasing energy. This convention is illustrated by the energy level diagram of the low-lying electronic states of O₂ in Figure 2.6, taken from ref. [10].

2-2.3 Selection Rules for *E*1 transitions

In an atom or molecule, an electromagnetic wave, e.g. ultraviolet light, can induce an oscillating electric or magnetic moment. If the frequency of the induced moment is the same as the energy difference between one initial state $|i\rangle$ and one final state $|f\rangle$, the interaction between an atom or a molecule and the electromagnetic field is resonant. Typically, the amplitude of this moment is called the transition moment, where the strongest transition is the electric dipole transition E1. The perturbation caused by the electric dipole interaction with an electric field $\vec{\mathcal{E}}$ is the inner product of $\vec{\mathcal{E}}$ with the dipole moment $\hat{\mu}$ and is given by:

$$H_{E1} = \hat{\boldsymbol{\mu}} \cdot \vec{\mathcal{E}} = -e\mathcal{E}_0 \ \hat{\boldsymbol{\varepsilon}} \cdot \hat{\mathbf{r}}$$
(2.22)

where e is the electron charge, $\hat{\mathbf{r}}$ is the position vector, and $\hat{\boldsymbol{\varepsilon}}$ is the electric polarization vector. The amplitude of the E1 perturbation between an initial state $|i\rangle$ and a final state $|f\rangle$ is:

$$\langle f | H_{E1} | i \rangle \propto \hat{\boldsymbol{\varepsilon}} \langle f | \hat{\mathbf{r}} | i \rangle$$
 (2.23)

Thus the intensity of the electric dipole transition E1 is proportional to the absolute value of the electric dipole transition moment μ_{fi} :

$$\boldsymbol{\mu}_{fi} = \langle f | \, \hat{\boldsymbol{\mu}} \, | i \rangle \tag{2.24}$$

where $\hat{\mu} = -e\hat{\mathbf{r}}$ is the electric dipole moment operator. The electric dipole transition moment can give a measure of the magnitude of the dipolar migration of charge that accompanies the transition. Therefore, Eq. 2.24 could be used to examine if a transition could occur and to formulate selection rules based on the integral. If the integral is zero then the transmission is forbidden, otherwise is allowed.

The selection rules in diatomic molecules for E1 transitions by using the notation of Eq. 2.21 are summarised below. These rules are established by detailed consideration of the symmetry properties of the electric dipole transition moment:

- (i) The parity must change $(g \leftrightarrow u)$ for centrosymmetric molecules that are following the inversion operation $\hat{i}\psi_e = \pm\psi_e$. Transitions such as ${}^{1}\Pi_g \rightarrow {}^{1}\Pi_u$, ${}^{1}\Sigma_u^+ \rightarrow {}^{1}\Sigma_g^+$, are allowed.
- (ii) $\Sigma^+ \to \Sigma^+$, $\Sigma^- \to \Sigma^-$ are allowed but not $\Sigma^+ \to \Sigma^-$, $\Sigma^- \to \Sigma^+$. This selection rule is a consequence of the μ_z transition dipole moment component which has Σ^+ symmetry.
- (iii) $\Delta \Lambda = 0$, ± 1 and $\Delta \Omega = 0$, ± 1 . The transitions $\Sigma \to \Sigma$, $\Pi \to \Sigma$, $\Pi \to \Delta$ and so forth are allowed.
- (iv) $\Delta S = 0$, $\Delta \Sigma = 0$. Transitions that change multiplicity are very weak for molecules formed from light atoms, but as spin-orbit coupling increases in heavy atoms as in Hund's case (c) transitions, $\Delta S \neq 0$ become more strongly allowed.
- (v) $\Delta J = 0, \pm 1$ but not $J = 0 \rightarrow J = 0$ and for $\Omega = 0 \rightarrow \Omega = 0, \Delta J \neq 0$

The first selection rule is a consequence of the fact that the transition dipole moment has odd parity and the subscripts g (gerade) and u (ungerade) even and odd in german respectively, are only used to classify the electronic states of homonuclear molecules. As for the second rule, the superscript + and - signs are attached only to diatomic Σ states depending of the results of the reflection operator $\hat{\sigma}_v$ around the internuclear axis, such that:

$$\hat{\sigma}_v \psi_e = \pm \psi_e$$

For higher states than Σ , there are an infinite number of planes containing the internuclear axis and hence there are an infinite number of possible reflections. For any of these planes, molecular terms with $\Lambda > 0$ always have a state which is symmetric (+) with respect to this reflection and one state that is antisymmetric (-), e.g. the symbol ${}^{2}\Pi^{\pm}$ the \pm is omitted.

The last selection rule is known as the rotational selection rule, where $\Delta J = \pm 1$ because of the conservation of angular momentum, and the molecule interacts with a photon that has unity quantised angular momentum. During the interaction, the angular momentum is forbidden to change by more than one unit. The transitions with $\Delta J = 1$ are defined as R branch transitions and the transitions with $\Delta J = -1$ are defined as P branch transitions. The transitions with $\Delta J = 0$ are defined as Qbranch transitions, and they are allowed only when the molecule possesses angular momentum parallel to the internuclear axis where $\Lambda \neq 0$ corresponding to terms higher than Π .

2-2.4 Vibronic Transitions

Vibronic transitions are simultaneous non-separated electronic and vibrational transitions that can explain why some forbidden electronic transitions can been observed. Figure 2.7 illustrates an example of a vibronic transition, where two molecular potential energy surfaces for two electronic states (X and A) of a diatomic molecule are being involved. The upper PES is typically displaced to the right relative to the lower PES because excitation of electrons generally introduces more antibonding character into the molecular orbitals, and the equilibrium bond length increases. Vibronic transitions are vertical transitions, meaning that the transition occurs from the initial internuclear distance R_e of the X ground electronic state and terminates at a turning point of the excited state A at the same internuclear distance R_e . The Franck -Condon classical mechanics principle can explain vertical transitions by considering that nuclear mass is so much larger than the mass of an electron, and as a result of



Figure 2.7: Illustration of an electronic transition that couples with a vibrational transition, resulting in a vibronic transition

this electrons are interacting first and rapidly with the incident photon giving the electronic transitions. Afterwards, the electronic transition is terminated where a vertical line cuts through the upper PES and the excited molecule is at a turning point of a vibration, so the nuclei are stationary, and the internuclear separation is the same as it was initially. Thereafter, the molecule is in a nonequilibrium state and the nuclei are readjusting causing the vibrational transition.

As for the quantum view of the Franck-Condon principle, we could refine the vibronic transition as the transition that occurs from the ground vibrational state of the lower electronic state to the vibrational state that it most resembles in the upper electronic state. This can be justified by considering Eq. 2.24, where the $\hat{\mu}$ electric dipole moment operator, depends on the position and the charge of the electrons along with the position and charge of nuclei which are denoted as \mathbf{R}_s and $Z_s e$ respectively:

$$\hat{\boldsymbol{\mu}} = -e\sum_{i}\mathbf{r_{i}} + e\sum_{s}Z_{s}\mathbf{R_{s}} = \hat{\boldsymbol{\mu}}_{e} + \hat{\boldsymbol{\mu}}_{N}$$

Considering the orthogonality of the electronic wavefunctions ψ_e and by using the Born-Oppenheimer approximation, we could separate the electronic and vibrational

part $\psi = \psi_e \psi_{\nu}$, with the resulting transition moment to be:

$$\boldsymbol{\mu}_{fi} = \langle \psi_{f}^{*} | \, \hat{\boldsymbol{\mu}}_{e} + \hat{\boldsymbol{\mu}}_{N} | \psi_{i} \rangle = \langle \psi_{f,e'}^{*} \psi_{f,\nu'}^{*} | \, \hat{\boldsymbol{\mu}}_{e} | \psi_{i,e} \psi_{i,\nu} \rangle + \langle \psi_{f,e'}^{*} \psi_{f,\nu'}^{*} | \, \hat{\boldsymbol{\mu}}_{N} | \psi_{i,e} \psi_{i,\nu} \rangle$$

$$= \underbrace{\int_{\text{Franck-Condon factor}} \int_{\text{Franck-Condon factor}} \psi_{f,e'}^{*} \hat{\boldsymbol{\mu}}_{e} \psi_{i,e} d\tau_{e} + \underbrace{\int_{=0} \psi_{f,e'}^{*} \psi_{i,e} d\tau_{e}}_{=0} \int_{=0} \psi_{f,\nu'}^{*} \hat{\boldsymbol{\mu}}_{N} \psi_{i,\nu} d\tau_{N}$$

$$\mu_{fi} = \boldsymbol{\mu}_{e'e} S(\nu',\nu) \qquad (2.25)$$

The vibrational integral is labeled as Franck-Condon factor, $|S(\nu', \nu)|^2$, and its physical meaning is that for vibrational levels that have great overlap the transition dipole moment is larger than for vibrational levels with less overlap. This corresponds to the quantum Franck-Condon principle, and the relative intensity of an electronic transition depends on the Franck-Condon factor.

Notation

Vibronic notation depends on the normal modes of vibration which are a superposition of a limited number of fundamental motions. A linear molecule such as a diatomic molecule has 3n - 5 modes of vibration and in general a molecule with n atoms has 3n - 6 modes of vibration. The notation also shows the vibrational states involved in the transition, e.g. the 0-0 transition is the one where the initial state is the vibrational state $\nu = 0$ at the electronic ground state and goes to the vibrational state $\nu' = 0$ at the excited electronic state. This example is a pure electronic transition, Fig. 2.7 shows a vibronic transition involving one quantum of electronic energy and one quantum of vibrational energy and if the ν_1 is excited then the vibronic transition will be designated 1_0^1 :

number of normal vibration(
$$\nu_1$$
) $\longrightarrow 1^{1 \longleftarrow}_{0 \longleftarrow}$ ground state, $\nu' = 1$

2-3 Ultraviolet Photodissociation

Photodissociation or photolysis is the fragmentation of a molecule due to absorption of electromagnetic energy from incident photons. Our area of interest is ultraviolet (UV) photolysis. The electromagnetic energy of the light beam is converted into internal energy of the molecule and if it exceeds the binding energy of the molecule subsequently the molecule breaks apart. The process can be described in two steps



Figure 2.8: Schematic illustration of photodissociation with a single UV photon

as follows:

$$ABC + n\hbar\omega \to ABC^* \to A + BC$$
 (2.26)

where $\hbar\omega$ is the photon energy with frequency ω , n is the number of absorbed photons, and ABC^{*} represents the excited state of the molecule prior to the dissociation.

Figure 2.8 illustrates the simplest UV photodissociation of a diatomic molecule AB with energy E_i : the incident photon excites the molecule from ground to a higher electronic state with energy $E_f = E_i + \hbar \omega$. If the potential of the excited electronic state is repulsive along the intermolecular coordinate R_{AB} , the excited AB^{*} dissociates directly on a very short time scale. In the case of indirect photodissociation shown in Figure 2.9, shows two examples of indirect predissociation. In the first case in 2.9(a) is called electronic predissociation or Herzberg's type I predissociation [11] where the photon excites first to a binding electronic state and the excited molecule undergoes a radiationless transition (rt) from the binding to a repulsive state and subsequently dissociates. In the second case 2.9(b) illustrates vibrational predissociation or Herzberg's type II predissociation which is applied for polyatomic molecules, where the binding potential has a well and a barrier that blocks the dissociation channel. The barrier is a result from an avoided crossing with an higher electronic state. In this case the incident photon creates a resonance state in the potential well which decays either by tunneling (tn) or by internal energy redistribution (IVR) [11].



Figure 2.9: Schematic illustration of electronic (a) and vibrational (b) predissociation

2-3.1 Unimolecular and Bimolecular Reactions

Most processes of interest are simple two-body events that end with the particles departing from each other with a fixed amount of kinetic and internal energy. The elementary bimolecular reactions are:

chemical reactions:

$$A + BC \rightarrow ABC^* \rightarrow AB + C$$

inelastic scattering:

$$AB(\nu, J) + C \rightarrow ABC^* \rightarrow AB(\nu', J') + C$$

As for the unimolecular reactions the most common are listed below:

photoionization :
$$AB + n\hbar\omega \rightarrow AB^* \rightarrow AB^+ + e^-$$
 (2.27)

photodissociation :
$$AB + n\hbar\omega \rightarrow AB^* \rightarrow A + B$$
 (2.28)

where $AB(C)^*$ is a state-excited complex and $n\hbar\omega$ is the photon energy.

2-3.2 Angular Distributions and Vector Correlations

The quantities that can be measured in a photodissociation experiment can be categorised either as scalar quantities or either as vector quantities. The scalar quantities such as the product state distributions and the channel's branching ratio have a magnitude but no direction. However, since the electromagnetic field vector $\vec{\mathcal{E}}$ of the photolysis laser defines a specific direction in the laboratory frame, all vectors inherent to a photodissociation process can be measured relative to the electric field vector $\vec{\mathcal{E}}$ that corresponds to the polarization of the photolysis laser. The vectors of interest are:

- (1) The transition dipole moment function of the parent molecule, μ .
- (2) The recoil velocity of the fragments, \mathbf{v} .
- (3) The rotational angular momentum of the fragments, j.

The vector correlation that most concerns this thesis is the one between transition dipole moment $\boldsymbol{\mu}$ and the recoil velocity \mathbf{v} , which results into an anisotropic distribution of the photofragments [12]. The first step to illustrate this correlation is to consider that the polarization of the photolysis laser is linear and fixed in the laboratory frame, and the absorption of UV photons occurs through the coupling of $\boldsymbol{\mu}$ with $\vec{\mathcal{E}}$. Thereafter, a random ensemble of molecules will have a transition dipole moment $\boldsymbol{\mu}$ with random orientation with respect to $\vec{\mathcal{E}}$. The probability of absorption through an E1 electric dipole-allowed process is proportional to the absolute value of $|\boldsymbol{\mu} \cdot \vec{\mathcal{E}}|^2$. This will lead to an absorption selectivity, meaning that the laser will selectively interact with molecules which happen to be oriented such that their transition dipole moment lies parallel to $\vec{\mathcal{E}}$.

In the molecular frame, the recoil velocity vector \mathbf{v} has a fixed angular relationship to $\boldsymbol{\mu}$, for example a parent diatomic molecule will be always either parallel or perpendicular to $\boldsymbol{\mu}$. Consequently, if $\boldsymbol{\mu}$ is aligned in the laboratory frame and provided that the dissociation takes place rapidly enough so that the alignment of $\boldsymbol{\mu}$ is not lost, then the angular correlation between \mathbf{v} and $\boldsymbol{\mu}$ will be transformed into an angular correlation between \mathbf{v} and $\vec{\mathcal{E}}$. Zare [13] noted that the normalized angular distribution of photofragments should be given by:

$$I(\theta) = \frac{1}{4\pi} [1 + \beta P_2(\cos\theta)]$$
(2.29)

where $-1 \leq \beta \leq 2$ is the anisotropy parameter, P_2 is the second order Legendre polynomial and θ is the angle between $\vec{\mathcal{E}}$ and \mathbf{v} . The limiting values of the anisotropy parameter β could reveal information regarding the symmetry of the electronic states involved in the dissociation of the parent molecule; i.e. if $\beta = 2$ then $I(\theta)$ anisotropy will follow a so-called $\cos^2(\theta)$ distribution which peaks at $\theta = 0$, indicating that the fragments are recoiling along $\vec{\mathcal{E}}$. as expected for excited states of the parent molecule
with Λ (or $\Delta\Omega$) = 0 e.g. Σ states with μ aligned parallel to the molecular axis (parallel transition). As for $\beta = -1$, anisotropy will follow a so-called $\sin^2(\theta)$ distribution which peaks at $\theta = \pi/2$, and the states involved have Λ (or $\Delta\Omega$) = 1 e.g. Π states, with μ aligned perpendicular to the molecular axis (perpendicular transition). The third case, of $\beta = 0$ corresponds to an isotropic distribution where the dissociation is independent of the angle θ and the fragments are isotropically distributed.

The correlation between \mathbf{v} and $\vec{\mathcal{E}}$ can be hindered causing anisotropy loss because it depends on maintenance of the alignment between $\vec{\mathcal{E}}$ and μ during absorption and fragmentation. Thus, factors such as rotation prior to dissociation, the lifetime, rotational temperature, and rotational constants of the parent molecule could lead to the loss of the anisotropy. A second vector correlation that leads to *orientation* and *alignment* of the nascent fragment, is between the transition dipole moment μ and the angular momentum vector \mathbf{j} . This correlation concerns the direction of \mathbf{j} with respect to the space-fix laser polarization $\vec{\mathcal{E}}$. The projection of \mathbf{j} on the $\vec{\mathcal{E}}$ axis is quantized by the quantum number $m_j = -j, -j+1, \ldots, j-1, j$ and the distribution $P(m_j)$ is a measure of the average angle between \mathbf{j} and $\vec{\mathcal{E}}$. If the distribution $P(m_j)$ is symmetric with respect to $m_j = 0$ then the molecule is aligned and if $P(m_j)$ is not symmetric with respect to $m_j = 0$ then the molecule is oriented.

2-3.3 Resonance Enhanced Multi-Photon Ionization (REMPI)

The Ionization Potential (IP) of most small molecules is above 8 eV, thus highly energetic photons are required to induce ionization through a direct one-photon absorption. This direct one-photon process has several drawbacks such as the need for expensive synchrotron sources and there is little state selectivity, i.e. the ionization of several vibrational and rotational states of the parent molecule ground electronic state will result into several electronic, vibrational, and rotational levels of the ion. Alternatively, these high energy states can be studied using multiphoton transitions and photons with wavelengths in the visible or near ultraviolet range.

Resonance Enhanced Multi-Photon Ionization (REMPI) is the most common multiphoton method, where laser sources that can provide high photon flux could match the resonant energy of the neutral parent molecule excited state by multiphoton absorption and then another photon could exceed the IP, resulting into ionization of the molecule . Usually three and four photons of the same frequency are used and are termed as (2 + 1) and (3 + 1) REMPI processes in which the first integer describes the number of photons required to reach the resonant level and the second integer shows the number of photons required to reach the IP limit from the resonant level. Depending on the molecule under study several REMPI schemes could be used such as the two-colour scheme, where photons of different frequencies are used. The notation for this scheme is (m + n') where as before m photons are required to reach the resonant level and n' photons with different frequency to ionize.

Chapter 3

Imaging Molecular Dynamics

In this section we will discuss how unimolecular reactions can be represented with Newton spheres based on energy and momentum conservation principles. We will describe the basic principles of ion imaging techniques and how ion images can be used for extracting insights of the aforementioned processes.

3-1 Newton Spheres

3-1.1 Kinetic Energy Release

Let us consider the photodissociation process described by Eq. 2.28, and by following the energy conservation principle we have that:

$$TKER = T_A + T_B = n\hbar\omega - D_0(AB) - E_{int}(A) - E_{int}(B)$$
(3.1)

where D_0 is the bond dissociation energy and E_{int} the fragment's internal energy. The conservation of momentum relates the momentum and thus the velocity vectors of the nascent fragments as:

$$m_A \mathbf{v}_A + m_B \mathbf{v}_B = 0 \tag{3.2}$$

Considering now that the dissociation process results into two nascent fragments flying with equal momentum in opposite directions in the centre-of-mass frame, we obtain the speed and kinetic energy ratios:

$$\frac{\upsilon_A}{\upsilon_B} = \frac{M_B}{M_A} = \frac{T_A}{T_B} \tag{3.3}$$



Figure 3.1: (a) A pair of Newton spheres for two dissociation events where $M_A < M_B$, (b) By summing up a large number of events for fragment B. From "Imaging in Molecular Dynamics, Technology and Applications" edited by Ben J. Whitaker, copyright Cambridge University Press.

Thus TKER is now related with the kinetic energy of the fragments as:

$$T_{A} = \frac{M_{B}}{M_{AB}} \times TKER$$

$$(3.4)$$

$$T_{B} = \frac{M_{A}}{M_{AB}} \times TKER$$

where the factor $\frac{M_B}{M_{AB}}$ or $\frac{M_A}{M_{AB}}$ is called the mass partitioning factor and indicates how the TKER is partitioned along the nascent fragments. In the case of photoionisation the photoelectron receives all TKER because the mass partitioning factor is $M_{e^-} \ll M_{AB^+}$, and as for the dissociation of homonuclear diatomic molecules such as the molecular oxygen O₂, the TKER is equally shared between the nascent O atoms.

The study of Kinetic Energy Release (KER) through equation 3.1 yields information on the bond dissociation energy and on the internal energy of the fragments. Internal energy involves several different aspects such as rotational, vibrational and electronic states and for that reason state selective detection schemes are usually employed. The most common is Resonant Multi-Photon Ionisation (REMPI) detection scheme where only those fragments that are in the probed state will be ionized and imaged.

3-1.2 Newton Spheres: Unimolecular Reactions

Figure 3.1 shows how Newton spheres are formed by multiple dissociation events. The parent molecule AB is located at the origin (x, y, z = 0, 0, 0) with no position spread $(\Delta x, \Delta y, \Delta z = 0, 0, 0)$ and zero initial velocity $(v_x, v_y, v_z = 0, 0, 0)$ and spread velocity $(\Delta v_x, \Delta v_y, \Delta v_z = 0, 0, 0)$. The first dissociation event sends fragments A upward and B downward, while event 2 sends the two fragments in opposite directions but with a different polar angle θ . Summing up for a large number of events 1, 2, 3, ... we see that each photodissociation yields fragments with the same speed but with varying directions. The summation creates spherical distributions in the velocity space the so-called Newton (velocity) spheres.

From the Newton spheres characteristics such as size and surface intensity pattern, one could extract information regarding the dissociation process. The size is directly proportional to the fragment's speed (scalar quantity) and the surface pattern shows the angular distribution (directionality) of the dissociation. If the intensity pattern has a maximum on the poles then a parallel transition ($\sim \cos^2 \theta$) along the parent molecule takes place, if it is most at the equator then a perpendicular transition ($\sim \sin^2 \theta$) takes place, and if the intensity is equally distributed on the surface of the sphere then an isotropic transition takes place. Furthermore, we could relate the obtained information from the Newton spheres for one species with that of its partner by just following energy and momentum conversation as we explained at section 3-1.1.

3-2 Ion Imaging

Ion imaging is a multiplex detection technique which allows the simultaneous measurement of rotational, vibrational, electronic and kinetic energy release of products of unimolecular and bimolecular reactions [6]. It was first demonstrated by Chandler and Houston in their pioneering study of 1987, "*Two-dimensional imaging of state-selected photodissociation products detected by multiphoton ionization*" published in the *Journal of Chemical Physics* [3]. Even though the energy resolution was limiting low around 15% - 20%, it was shown for the first time that ion imaging could be applied in the field of molecular reaction dynamics in order to obtain insights on the photodissociation dynamics. The key point for the utilisation of ion imaging was the advent of microchannel plate (MCP) particle multipliers and the commercial availability of CCD cameras in the 1980s.



Figure 3.2: General scheme of velocity map imaging setup.

Chandler and Houston have pioneered the use of Position-Sensitive Detector (PSD) consisting of a chevron-type pair of MCPs coupled to a phosphor screen and a charge-coupled-device (CCD) camera, to study photodissociation dynamics. Thereafter, the recorded two-dimensional projection of reaction products was used to reconstruct the full three-dimensional distribution by exploiting the inverse Abel transform [14]. Eppink and Parker introduced Velocity Map Imaging (VMI) that made a great improvement on the energy resolution by an order of magnitude to 2% - 5% [8]. Figure 3.2 shows the general scheme of VMI setup where the coordinate system is defined with the x and y axes parallel to the detector plane, and z perpendicular to it and coinciding with the symmetry axis. The fundamental idea of VMI is that if the charged particles are formed in a specially shaped electric field or the field is switched on at the right moment of time, they are accelerated towards the detector in such a way that their arrival positions and times depend on the initial velocities:

$$(\upsilon_x, \upsilon_y, \upsilon_z) \to (x, y, t) \tag{3.5}$$

Therefore, by using a PSD detector we are able to determined the initial velocity vector of the particle by measuring the event position on the detector (v_x, v_y) and the Time-of-Flight (TOF) (v_z) . The electric field is shaped in such way that the initial positions $\delta \mathbf{r}$ of the particles does not affect the velocity mapping. This could be achieved by introducing inhomogeneity in the extraction field that acts as an electro-

static lens and focuses the particles velocities onto the imaging plane. The "focusing" is important because the molecular beam has a finite width on the order of few millimeters. Thus dissociation takes place at different positions in the molecular beam and this spatial spread results to blurring of the image and limited velocity resolution. However, Abel transform requires an axis cylindrical symmetry parallel to the imaging plane that excludes studying scattering processes and two-colour experiments with different laser polarization geometries. Kitsopoulos and coworkers addressed the cylindrical symmetry issue by introducing Slice Imaging that exploits delayed pulse extraction to sufficiently expand the ion cloud in order to image its central part by "slicing" with the use of a narrow time-gate in front of the PSD detector [1, 15, 16].

3-2.1 Ion Optics

Time-of-Flight Mass Spectrometry

In Time-of-Flight Mass Spectrometry (TOF-MS) the essential principle is that a population of ions moving in the same direction and having a distribution of masses with a constant kinetic energy, will have a corresponding distribution of velocities in which velocity is inversely proportional to the square root of the mass-to-charge ratio m/z. Figure 3.3 shows the Wiley-McLaren TOF spectrometer [17], where an ion of mass m, charge q = ze, initial velocity v_i and total initial energy E_i is entering



Figure 3.3: Illustration of Wiley-McLaren TOF spectrometer geometry.

through the source region at the ionization region with length s and electric field $\vec{\mathcal{E}}_s$ with potential V_s , following by the acceleration region with length d and electric field $\vec{\mathcal{E}}_d$ with potential V_d and thereafter is the field-free region with length D that ends at the MCP detector.

The ion acquires energy as follows:

$$E = E_i + qV_s + qV_d \tag{3.6}$$

and the time-of-flight is given by:

$$TOF(s_0, E_i) = t_s + t_d + t_D$$
 (3.7)

where the each region TOF can be easily deduced by the equation of motion $s = s_0 + v_i t + \frac{1}{2} (qV_s/ms_0)t^2$

$$t_{s} = \sqrt{\frac{2m}{q}} \frac{s}{V_{s}} (\sqrt{E_{i} + qV_{s}} \pm \sqrt{E_{i}})$$

$$t_{d} = \sqrt{\frac{2m}{q}} \frac{d}{V_{d}} (\sqrt{E_{i}} \pm \sqrt{E_{i} + qV_{s}})$$

$$t_{D} = \sqrt{\frac{2m}{q}} \frac{D}{2\sqrt{E_{i}}}$$
(3.8)

Mass-to-charge ratios (m/z) are determined by measuring the time that ions take to move through a field-free region between the source and the detector. At the field-free region the electric potential energy is converted into kinetic energy

$$E_{kin} = \frac{1}{2}mv^2 = E_{el} = qV_s$$
 (3.9)

Thus the velocity of the ion leaving the source region is

$$v = (\frac{2qV_s}{m})^{1/2} \tag{3.10}$$

The time t_D needed to cover the field-free region is

$$t_D = \frac{D}{v}$$

Finally

$$t_D = \sqrt{\frac{m}{q} \left(\frac{D^2}{2V_s}\right)} = D\sqrt{\frac{m}{2qV_s}}$$
(3.11)

Space-Focusing

The first electrode arrangement capable of space-focusing was given by Wiley and McLaren in their 1955 seminal paper [17]. Space-focusing was applied in order to address the initial position problem in mass spectrometry (or initial spatial spread), in which particles that are ionized in different places of the ionization volume arrive at different times at the detector. A particle that is closer to the detector will gain less energy and it will arrive at the same time with an identical particle that it was positioned further (greater acceleration) from the detector. If we define:

$$U = qV_s + qV_d; \quad k_0 = (s_0V_s + dV_d)/s_0V_s \tag{3.12}$$

and consider the *TOF* when $s = s_0$ and $E_i = 0$, from a substitution of Eqs. 3.8 and 3.12 into Eq. 3.7 we have that:

$$TOF(0, s_0) = \sqrt{\frac{m}{2U}} \left(2\sqrt{k_0} s_0 + \frac{2\sqrt{k_0}}{\sqrt{k_0} + 1} d + D \right)$$
(3.13)

By setting the first and the second partial derivative of $TOF(0, s_0)$ with respect to s_0 equal to zero we have the following space-focusing condition:

$$D = 2s_0 k_0^{3/2} \left(1 - \frac{1}{k_0 + k_0^{1/2}} \frac{d}{s_0} \right)$$
(3.14)

By substituting the dimensions of the apparatus we can deduce from Eqs. 3.14 and 3.13 the ratio V_d/V_s needed in order to achieve space-focusing.

Time-Lag Focusing

The other important issue in TOF mass spectrometry that was addressed also by Wiley and McLaren is the initial velocity dispersion, i.e. identical particles with different initial velocity will arrive at different times to the detector. They proposed *time-lag focusing* in which two ions formed at the same initial position s and are moving with equal and opposite velocities. The one moving towards the repeller will need a so-called "turn-around" time to stop and reaccelerate back to its initial position in order to have an identical motion with the second ion. However, the first ion will *lag* by the *turn-around* time τ and to reduce this initial kinetic energy (velocity) the ions are first allowed to expand into a field-free region in the source and after a certain time equal to the time-lag, an electric field is applied to extract the ions outside the source [17]. Turn-around time can be deduced from the velocity principle

$$v = v_i + \frac{sV_sq}{m}t; \quad t = \frac{v - v_i}{sV_s}\frac{m}{q}$$
(3.15)

and by setting $v_i = -v$

$$\Delta \tau = \frac{2|v_i|m}{sV_s q} \tag{3.16}$$

Substituting velocity with initial kinetic energy $v_i = \sqrt{2U_0/m}$ we obtained the turnaround time $\Delta \tau$

$$\Delta \tau = 2 \frac{2mU_0}{sV_s q} \tag{3.17}$$

Is obvious that we can reduce the turn-around time by increasing the strength of the electric field and by lengthening the field-free region in order to make the turn-around time smaller relative to the total TOF. Wiley and McLaren have proposed the time-lag focusing in which, the ionization region is to be confined to a small area very close to the extractor plate (< 2 mm) such that the spatial focus of the ion cloud to be at the detector and by allowing a time lag equal to the one-half of the turn between ionization and extraction the ions are spreading out. The resulting large spatial ion distribution is refocused by the space-focusing technique as described before. However, time-lag focusing has drawbacks related with the design of the spectrometer because of the demand for a very small ionization area and also it is mass dependent therefore can be applied only on a limited mass range.

3-3 Velocity Map Imaging (VMI)

3-3.1 VMI Ion Optics: Radial Focusing

The VMI ion optics configuration is very similar to the Wiley-McLaren arrangement as shown in Fig. 3.4, the only difference is that for VMI the two grids are replaced by a pair of flat electrodes with a circular opening of finite radius, forming an aperture electrostatic lens. The VMI detection is achieved by adjusting the voltage difference between the two electrodes in order to obtain potential contours that are the optical analogy of a lens and will focus ion velocities onto the imaging plane of the detector.

Figure 3.4 shows the ion optics configuration with the electrostatic lens used for VMI studies of a skimmed molecular beam that passes through a small hole in the repeller (R) plate. Ions are formed between the repeller and the extractor (E) by counter-propagarting laser beams for two-colour photodissociation experiments and



Figure 3.4: Illustration of VMI ion optics for radial focusing with the field lines for the electrostatic lens. Ion trajectories are shown in blue for v_0 parallel to the z-axis and in black for v_0 perpendicular to it.

then are accelerated past the ground (G) electrode and fly through the time-of-flight tube to the detector. The repeller and extractor are flat annular electrodes spaced 15 mm apart with 20 mm open inner diameters and the flight tube has a length of 360 mm.

The VMI principle as mentioned in Eq. 3.5 and in Fig. 3.2, is mapping the initial velocity of ions and assuming that they are formed by a photodissociation experiment on the y-direction then the ion Newton sphere crushes as a disk of a radius r on the detector. Most of the ions are lying at the outer edge of the disk and the radius of it can be easily deduced by using Eq. 3.11 for time-of-flight:

$$r \approx v_y \times TOF \approx D(KE/qV_R)^{1/2}$$
 (3.18)

where KE is the kinetic energy, D is the free-field tube length, q the particle charge and V is the repeller voltage. This massless relation implies that the \sqrt{KE} is mapped instead of velocity or momentum, in other words if we time-gated the detector to be ON for a mass with a corresponding t_{TOF} , any species with the same kinetic energy will appear at the same radius r on the detector.

3-3.2 Reconstruction Methods

The two-dimensional projection of the Newton sphere P(x, y) can be described as one-dimensional P(r) because of the cylindrical symmetry, where $r = \sqrt{x^2 + y^2}$ as shown in Fig. 3.2. If we use just one row of the recorded image corresponding to a line at a distance x_0 from the origin then the projection can be expressed as:

$$P(x,y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I(x,y)\delta(x-x_0)dxdy = 2\int_{0}^{\infty} I(x_0,y)dy$$
(3.19)

Changing coordinates by using $y = \sqrt{r^2 - x^2}$ we have $dy = rdr/\sqrt{r^2 - x^2}$

$$P(r) = 2 \int_{x}^{\infty} \frac{I(r)rdr}{\sqrt{r^2 - x^2}}$$
(3.20)

The above relation is known as the *Abel-transform* and by using inverse transform we can recover the initial distribution from the measured projection

$$S(r) = -\frac{1}{\pi} \int_{r}^{\infty} \frac{dP(x)}{dx} \frac{dx}{\sqrt{x^2 - r^2}}$$
(3.21)

Solving Eq. 3.21 is a demanding task because of the singularity at $x^2 = r^2$ and the derivative tends to magnify the noise. Furthermore, the initial distribution of photofragments could exhibit some degree of asymmetry because of a mismatch between the ionization laser bandwidth and the Doppler profile of the fragments that will result into image distortion. Two main approaches have been developed: the inversion methods and the forward convolution methods with a great number of underlying methods (Fourier-Hankel, onion peeling, BASEX). However, there are several issues in reconstructing the three-dimensional velocity distribution that can not be addressed with these mathematical transformations [5, chapter 3].

3-3.3 VMI Data Analysis

In the previous subsection we described the reconstruction of the initial velocity distribution based on the inverse Abel transform. Generally, the input to the reconstruction method is each row of pixels that corresponds to two-dimensional ring projections. The result is a slice through the center of the original three-dimensional distribution, which is the reconstructed image and a sum of concentric rings corresponding to each crushed Newton sphere. The reconstructed images are enclosing a large amount of information and their properties, e.g. its radius, angle and intensity are related with the reaction under study. The radial position is a direct measurement of the nascent fragment's kinetic energy and can elucidate the reaction channels or even unveil new system energetics. The angular pattern of the reconstructed rings is directly related with the surface pattern of the Newton spheres and by studying the angular distribution we can obtain the differential cross section $d\sigma/d\Omega$, vector properties (e.g. anisotropy parameter β) and possible vector correlations as explained in sections 2-3.2 and 3-1.2. And from image intensities we could get a direct measure of the population, or number density, for each product energy and angle.

Kinetic Energy Release

In this subsection we will describe the methods for obtaining speed distributions, kinetic energy release (KER) and angular distributions from the reconstructed image $S(r, \theta)$. The speed distribution P(v) of the photofragments is defined as the total amount of photofragments with speed v and is found by integrating the acquired Abel-transformed image over all angles, as follows:

$$P(\upsilon)dr = \int_{0}^{2\pi} \int_{0}^{\pi} S(r,\theta) \underbrace{r^2 \sin \theta d\phi d\theta dr}_{\text{Jacobian}}$$

The image is a two-dimensional ring distribution so does not dependent on the azimuthal angle ϕ because of the cylindrical symmetry:

$$P(\upsilon)dr = 2\pi \int_{0}^{\pi} S(r,\theta) \underbrace{r^{2} \sin \theta d\theta dr}_{\text{Jacobian}}$$
(3.22)

In order to obtain the speed distribution, we have to relate the distance r from the symmetry axis to the radius ρ which is the distance from the image center (center-of-mass of the reaction) and is directly proportional to the velocity of photofragments as follows:

$$r = \rho \sin \theta \tag{3.23}$$

By inserting Eq. 3.23 into Eq. 3.22 we have:

$$P(\upsilon) = 2\pi\rho \int_{0}^{\pi} S(\rho,\theta)\rho\sin\theta d\theta \qquad (3.24)$$

Each row of the image has an area of pixels $2\pi\rho d\rho$, thus the speed distribution is proportional to:

$$P(v) \propto \int_{0}^{\pi} \underbrace{\rho \sin \theta}_{\text{weighting factor}} S(\rho, \theta) d\theta \qquad (3.25)$$

It is also possible to determine the speed distribution for a specific range of ejection angles by changing the integration limits to $(\theta_{min}, \theta_{max})$.

As for obtaining KER, we know that the pixel position is proportional to $\sqrt{E_{kin}}$, thus we can relate the kinetic energy with pixels as follows:

$$E_{kin} = \frac{1}{2}m\upsilon^2 = k_{cal}pix^2 \tag{3.26}$$

where k_{cal} is a calibration factor with energy units that is dependent on the experiment parameters such as repeller voltage and the spatial position of the photolysis laser.

Angular Distribution

The angular distribution (or differential cross section) is defined as

$$\frac{d\sigma}{d\Omega} = \frac{\text{Number of fragments scattered into the solid angle } d\Omega \text{ per unit time}}{\text{Intensity of the incident beam}}$$

where the solid angle is defined as:

$$d\Omega = \frac{dA}{\rho^2} = \sin\theta d\theta d\phi \tag{3.27}$$

where the area element $dA = \rho^2 \sin \theta d\theta d\phi$ for spherical coordinates. Let the number of fragments scattering into an angle $d\theta$ be denoted as $N(\theta)$. Then the number of fragments $N(\Omega)$ scattering into a solid angle $d\Omega$ is given by:

$$N(\Omega) = N(\theta) \sin \theta d\phi$$

Using the above relationships with the assumption that the incident beam has unity intensity, thus the angular distribution can be rewritten as:

$$\frac{d\sigma}{d\Omega} = \frac{N(\Omega)}{d\Omega} = \frac{N(\theta)}{d\theta}$$
(3.28)

Eq. 3.28 indicates that the angular distribution can be obtained by integrating in a certain range of speed values (pixels) that corresponds to radial sectors centered at

the center-of-mass of the reaction. Usually, we choose the full-width half-maximum (FWHM) of each reaction channel in the KER as integration limits.

3-3.4 VMI Experiment

In a nutshell, the VMI experiment for measuring Newton spheres for unimolecular reactions, involves the following experimental steps:

- (i) Photodissociation of molecules in a molecular beam using a linearly polarized laser with the polarization direction parallel to the detector plane.
- (ii) Conversion of the photofragments into ions by a state-selective REMPI scheme by using a second laser (colour) with polarization parallell to the detector plane.
- (iii) Projection of the ion spheres onto a two-dimensional detector which is timegated to detect the mass (m/z) of interest.
- (iv) Mathematical transformation of the two-dimensional projection back to the central slice of the three-dimensional velocity distribution of step (i) and subsequent analysis for speed distribution and angular distribution extraction.

We can make a short-list of the most important photodissociation properties that we could quantify, as a function of excitation wavelength of a hypothetical diatomic molecule AB that is excited via three different pathways a, b and c with nascent photofragments A and B (internal states i, j and k) as shown in Fig. 3.5. Multiple scenarios can be made on the three different pathways: (a) Direct excitation from a $\mathbf{X}(\Sigma)$ ground state to a repulsive state $\mathbf{A}(\Sigma)$ correlating to the first dissociation channel A + B(i). (b) Excitation to the repulsive wall of state $\mathbf{B}(\Pi)$, to a bound state correlating with the second dissociation channel A + B(j). Curve crossing to the first channel via the repulsive state is possible. (c) Excitation to a bound state $\mathbf{C}(\Sigma)$ correlating to the third dissociation channel A + B(k). Predissociation can take place by curve crossing via another repulsive state leading to the second channel.

- D₀, the A − B bond energy of the X state, and of the B and C bound excited states such as those reached by pathways b and c.
- The symmetry $(\Sigma, \Pi, \Delta, \ldots)$ of the ground and excited states.
- The absorption cross-sections $(\sigma_a, \sigma_b, \sigma_c)$ for each transition.
- Time-scales for (pre-)dissociation of each quantum level of the excited states.



Figure 3.5: Potential energy surfaces for different types of photodissociation pathways.

- Product yields to the first, second and third dissociation channels.
- Angular distributions (beta parameter, β and higher parameters) and possible vector correlations for each dissociation channel.
- Characterization of the importance of **curve crossing** from the photoexcited curve to curves leading to other dissociation products.
- Characterization of the importance of **coherent** (a + b + c) versus incoherent (a, b or c) excitation of the different pathways.

3-4 Slice Imaging

The advantages of recording the central slice of the Newton sphere that contains the full angular and translational energy information instead of crushing the full threedimensional sphere were obvious because of the limitations induced by the detection conditions. For example, in a two-colour experiment the presence of a three-vector correlation can remove the azimuthal symmetry and this makes information from the Abel transformation invalid. Gebhardt et al. they addressed the issue by introducing *Slice Imaging* in 2001 [1], in order to expand the VMI applications on experiments without the requirement of an cylindrical symmetry axis parallel to the imaging plane. The motivation was the study of vector correlations in angular momentum alignment and/or orientation where non-cylindrically symmetric slice images are offering the ability to measure photofragment polarization parameters such as $Im[a_1^{(k)}(\perp, \parallel)]$ [18, 19]. Since then several approaches for slice imaging have been developed such as *Direct Current (DC) Slice Imaging* [15, 16], *Single Field Slice Imaging* [20] and *Optical Slice Imaging* [16, 21, 22].

3-4.1 Concept

In previous sections we described the basic concept of TOF-MS and VMI, the timelag focusing and the VMI radial focusing. The latter is exploited also in slicing by mounting an Einzel lens behind the extractor as shown in Fig. 3.6 to velocity map the photofragments $(v_x, v_y) \rightarrow (x, y)$ on the detector, with the third velocity component to be mapped to the ion time-of-flight $(v_z \rightarrow t)$. The former is used in slicing in the analogous form of pulsed delay extraction [1] and as we described it first was used in TOF-MS in order to improve mass resolution and to reduce the initial velocity spread [17]. However, the operating conditions were such that the spatial focus of the ion cloud occurred at the detector, and in the case of slicing we want to achieve the maximal possible spread of the ion cloud. The spatial spread is achieved by introducing a time-delay τ following the photolysis and fragments ionization in which both repeller and extractor have equal potential (field-free conditions). As we have seen in Section 3-2.1 the time-of-flight for a Wiley-McLaren spectrometer that contains two accelerating regions is given by Eq. 3.8, and if a single uniform acceleration field (V_s) is used then the TOF is given by:

$$T(s, E_i) = t_s + t_D = \sqrt{\frac{2m}{q}} \frac{s}{V_s} (\sqrt{E_i \pm qV_s} \pm \sqrt{E_i}) + \sqrt{\frac{2m}{q}} \frac{D}{2\sqrt{E_i}}$$
(3.29)

where the \pm symbol shows the initial direction of fragments, i.e. (+) for forward scattered fragments s_f moving towards the detector and (-) for for backward scattered fragments s_b moving away from the detector. Gebhardt et al. have shown that the Newton sphere will always crush along the TOF axis with the vertical dimension (Δy) of the ion cloud continuously increasing during its drift time towards the detector, and the horizontal spread (Δx) to be nearly invariant. For that reason they proposed the use of delay pulsed extraction, in which dissociation and ionization are taking place in field-free conditions and the extraction field is pulsed on after time τ .



Figure 3.6: Scale schematic of the ion optics used in slice imaging. From ref. [1].



Figure 3.7: (a) The upper panel depicts the spatial evolution of the ion cloud on its way to the detector for the case of a delayed extraction field ($\tau = 250 ns$). The simulation has been performed for ground-state Cl from the photodissociation of Cl₂ at 355 nm (c = 1240 m/s, $v_0 = 1700$ m/s, L = 45 cm, $s_0 = d_0 = 1$ cm, E = 333 V/cm). The dotted circle is given to emphasize the distortion of the ion cloud by the acceleration. A space focus appears in the drift region after which the axial width of the ion cloud increases rapidly. (b) The lower panel shows the time width of the ion cloud at the detector as function of the photofragment velocity v_0 and the different curves correspond to different delay times τ . From ref. [1].

The position of the ions with respect to the extractor grid are:

$$s = s_0 - c\tau$$

$$s_f = s_0 - v_i\tau$$

$$s_b = s_0 + v_i\tau$$
(3.30)

where the initial velocity v_i is equal to the sum of the molecular beam velocity c plus the velocity of the photofragments v_0 and α is the angle between the direction of the photofragments and the TOF axis $v_i = c + v_0 \cos \alpha$. In this case the temporal spread of the ion cloud along the TOF axis becomes:

$$\Delta T = |T_f(s_f, v_f) - T_b(s_b, v_b)|$$
(3.31)

The influence of the extraction delay τ on the spatial evolution of the ion cloud is shown in Fig. 3.7(a), for the upper panel the delay extraction was set to $\tau = 250 ns$, and from the simulation (Fig. 3.7(b)) is apparent that a space focus appears in the free-field region after which the axial width on the ion cloud increases rapidly. Thus, the extraction delay can be used as a handle for controlling the ion cloud size along the TOF axis in order to ensure that the perpendicular dimension of it does not exceed the detector diameter. The choice of how much extraction delay is needed in each case is empirical and typically slicing requires a value of about $\Delta T = 500 ns$ for the ion cloud temporal spread [1]. Thereafter, the ion cloud central section is sliced by a narrow time-gate (~ 40 ns) and acquired by a MCP detector.

As for the dc slicing approach, it was introduced by two concurrent and independent studies and the main difference with the original slice imaging is the use of a weak dc extraction field instead of a pulsed delay extraction in order to achieve the temporal spreading required for slicing [15, 16]. The two studies they were implemented by Townsend et al. [16] with a four-plate ion optics and by Lin et al. [15] with a multiplate ion optics set and in both cases the weak extraction field is followed by a strong acceleration field. The newest variant of slice imaging is using a single acceleration field by utilizing a two-electrode geometry with a step added in order to achieve the focusing conditions needed for velocity mapping [20]. This configuration gives the advantage of meeting the focusing conditions by translating the laser position along the TOF axis instead of adjusting the voltage ratio between electrodes as in the case of VMI.



Figure 3.8: A very finite strip of the two concentric Newton spheres central section made on the azimuthal symmetry axis.

3-4.2 Slice Images Analysis

Slice images are the central slice $(v_z = 0)$ of the Newton sphere that contains all the required information. If the sliced function $S(v_z)$ is centered at $v_z = 0$ by time-gating the detector in order to obtain projections of a very finite stripe of the Newton sphere, as is shown in Fig. 3.8 then the measured sliced projection is:

$$P(x,y) = \int_{-\infty}^{\infty} I(\upsilon_x, \upsilon_y, \upsilon_z) S(\upsilon_z) d\upsilon_z \approx I(\upsilon_x, \upsilon_y, 0) \Delta \upsilon_z = I(\upsilon_x, \upsilon_y, 0)$$
(3.32)

where Δv_z is the slice thickness, and if the slice is thin enough the initial distribution can be obtained immediately.

Extracting the speed distribution from slice images is analogous to the method described in section 3-3.3 for VMI images. The azimuthal contribution to the solid angle must be excluded from the integration in Eq. 3.24 which is equal with 2π , and the weighting factor $\rho \sin \theta$ remains the same as in the case of VMI images. As for the angular distribution it is obtained exactly the same manner as in the case of VMI images with the only difference being the normalization with the respective

opposite polarization image, e.g. if an image has been obtained with laser polarization parallel to the imaging plane (XX) its angular distribution has to be normalized with an angular distribution from an image with laser polarization perpendicular to the imaging plane (ZZ).

3-4.3 Single-Field Slicing Experiment

A typical slicing experiment starts by forming a molecular beam of the molecule of interest seeded either in He or Xe and supersonically expanded through a homemade piezoelectrically actuated nozzle valve (1 mm diameter). After passing through a skimmer, the molecular beam is intersected at right angles by the photolysis and photofragment ionization lasers at the geometric focus position of a single-electrode repeller-grid arrangement with a diameter hole ~ 2 mm [20]. Then the repeller is pulsed ON at the appropriate time delay (for ³⁵Cl is typically ~ 200ns and for ¹²⁷I is ~ 300ns) following the photolysis and ionization.

The photofragments traverse a field-free time-of-flight region (45 cm) and are detected by a gated, position-sensitive detector (dual, imaging-quality MCP array coupled to a phosphor screen) imaging the center slice of the photofragment sphere. The image frame is recorded asynchronously every second (~ 10 laser shots) by a charge coupled device camera (CCD) and typically ~ 3000 such frames are averaged to form signal images. Background images are recorded with the molecular beam OFF and subtracted from the signal images. As described above, each final image is integrated from its center over angle to extract the speed and over radius to extract the angular distributions of the photofragments.

Chapter 4

Molecular Beams and Cluster Formation

The formation of clusters in gas expansions into vacuum was first observed in the mid 1950s by Becker et al. [23] by sampling the core of a condensing supersonic nozzle flow. Since that time condensation of such free-expansions has been widely used to produce clusters, i.e. aggregates of rare gases or closed-shell molecules with sizes ranging from dimers up to many thousand monomers [24]. Numerous applications of atomic or molecular clusters have been developed and a great number of new methods for clusters generation can be found in the literature such as supersonic jets, gas aggregation, sputtering, laser ablation and cluster aggregation [25].

Gas dynamics are used to understand the properties of the nozzle beams and we will focus on the free-jet supersonic expansion. First we will give some fundamentals of gas dynamics, such as thermodynamic relations and principles of one-dimensional flow. Then a description of the adiabatic supersonic expansion through a nozzle into vacuum, that leads to a drastic temperature decrease in the molecular beam and subsequently into cluster formation, will be given. Due to the lack of a rigorous theory, cluster formation is explained by semiempirical scaling laws, derived using general considerations about the kinetics of condensation and its dependence on the initial expansion conditions [24, 26, 27].

4-1 Fundamentals of Gas Dynamics

4-1.1 Fundamentals of Gas Dynamics: Introduction

The formation of molecular beams can be classified as either effusive beams or nozzle beams, based on the number of collisions between the molecules during the expansion. The *Knudsen number* K_n is used, which is defined as the ratio of the mean free path over the length L, the aperture size in the case of nozzle beams. For the case of effusive beams, Knudsen number is $K_n \gg 1$ meaning that there are no collisions in the aperture vicinity, and as for case the of molecular beams Knudsen number is $K_n \ll 1$, meaning that there are many collisions during the expansion. Therefore the speed distribution of nozzle beams is rather narrow, its maximum is shifted to higher velocities and molecules experience a considerable reduction of their rotational temperature.

4-1.2 Fundamentals of Gas Dynamics: Thermodynamic Relations

The equation of state of an ideal gas is defined as:

$$P = \frac{R}{M}\rho T \tag{4.1}$$

where R is the ideal gas constant, M the molar mass, ρ the density and T the temperature of the ideal gas. The first law of thermodynamics states that the heat dq transferred to the unit mass of a gas at constant pressure P and constant number of molecules is:

$$dq = de + P \ d\left(\frac{1}{\rho}\right) \tag{4.2}$$

where e is the internal energy (rotation, vibration, electronic) per unit mass. The enthalpy h is defined as:

$$h = e + \frac{P}{\rho} = e + \frac{RT}{M} \tag{4.3}$$

Using the this relationship we can relate the heat transfer in the case of an ideal gas with enthalpy:

$$dq = dh - \frac{1}{\rho}dP \tag{4.4}$$

The specific heats c_V and c_P corresponding to constant-volume and constant-pressure heating respectively, are given by:

$$c_V = \left(\frac{\partial e}{\partial T}\right)_V, \qquad c_P = \left(\frac{\partial h}{\partial T}\right)_P$$

Thus

$$c_P = c_V + \frac{R}{M} \tag{4.5}$$

and by inserting the specific heat ratio $\gamma = c_P/c_V$ we obtain:

$$c_V = \frac{1}{\gamma - 1} \frac{R}{M}, \qquad c_P = \frac{\gamma}{\gamma - 1} \frac{R}{M}$$
(4.6)

Isentropic flow processes, which take place at constant entropy s without exchange of heat between the gas and its surroundings (dq = 0), are of great importance in gas dynamics. For these processes we have that:

$$\frac{1}{\gamma - 1}\frac{dT}{T} - \frac{d\rho}{\rho} = 0, \qquad \frac{\gamma}{\gamma - 1}\frac{dT}{T} - \frac{dP}{P} = 0$$
(4.7)

4-1.3 Fundamentals of Gas Dynamics: One-Dimensional Flow

One of the most important and most commonly employed simplifications is that the flow is one-dimensional. This means that all flow properties are uniform over every cross section of the flow passage and that is realized in tubes and nozzles if the rate of change for the cross-sectional area is small in the direction of flow. Thus the flow properties velocity of flow w, the density ρ , the pressure P and the temperature T depend only on one variable, the path length x measured in the flow direction. To calculate these functions, three conservation laws are available: conservation of mass (continuity equation), conservation of momentum (momentum equation), and conservation of energy (energy equation).

Continuity equation: Mass conservation requires the absence of spontaneous production or annihilation of mass in the flow field of surface A.

$$\frac{dw}{w} + \frac{d\rho}{\rho} + \frac{dA}{A} = 0 \tag{4.8}$$



Figure 4.1: Subsonic (left) and supersonic (right) propagation of a disturbance in a flowing medium.

Momentum equation: In the absence of external forces, we have

$$wdw = -\frac{dP}{\rho} \tag{4.9}$$

Energy equation: Energy conservation in a flowing gas means that the stored energy per unit mass, consisting of thermal, kinetic, and potential energy, must be constant in time. For steady flow, this can be expressed by

$$wdw + dh = 0 \tag{4.10}$$

Speed of Sound and Mach Number

The sonic speed c of an ideal gas is given by:

$$c = \sqrt{\gamma \frac{P}{\rho}} = \sqrt{\gamma \frac{RT}{M}}$$
(4.11)

Figure 4.1 shows the two cases for a propagation in a medium at subsonic flow (left side) and at supersonic flow (right side). In the case of subsonic flow (w < c) the disturbance propagates at $\tau = 0$ in all directions from its center as a spherical wave, but with different velocities in different directions. In the case of supersonic propagation (w > c) all spherical waves are confined to a given cone (Mach cone), while the space outside the cone is completely free of disturbances (Fig. 4.1). The conical separating surface forms a wave front, termed as *Mach wave*. The half-angle α of the

cone is called the Mach angle and is defined as

$$\sin \alpha = \frac{c}{w} = \frac{1}{M_a} \tag{4.12}$$

where M_a is the Mach number denoted as the ratio of the flow velocity to the local speed of sound. The physical significance of the Mach number follows from the fact that the velocity of sound is proportional to the mean molecular speed in a gas. Hence, the Mach number is a measure of the ratio of the directed motion of the flow to the random thermal molecular motion.

4-2 Free-jet Supersonic Expansion

As the molecular beam leaves the stagnation chamber through the nozzle, the pressure gradient across the nozzle at source pressure P_0 to the high vacuum region at P_b accelerates the flow. The degree of acceleration depends upon the pressure ratio P_0/P_b , but if this ratio exceeds a critical value G = 2.1 then the beam will become supersonic with a Mach number $M_{\alpha} > 1$ [25]. The critical value G is given by:

$$G = \left(\frac{(\gamma+1)}{2}\right)^{\gamma/(\gamma-1)} \tag{4.13}$$

where γ is the ratio of the gas specific heat (or adiabatic index) that can be related with the degrees of freedom (f) of a molecule by:

$$\gamma = 1 + \frac{2}{f} \tag{4.14}$$

and Table 4.1 shows the different values of γ .

monoatomic ideal gas
(frozen vibrations)diatomic
moleculesgas,
(frozenlinear
vibra-
vibra-
frequency vibrations)polyatomic molecules
(low
frequency vibrations)5/37/59/7

Table 4.1: Adiabatic index γ values.

Figure 4.2 illustrates the essential features of a supersonic jet expansion such as the stagnation pressure P_0 , initial temperature T_0 and the nozzle diameter d into a vacuum region of background pressure P_b . The gas accelerates in the nozzle throat to approximately sonic speed $M_{\alpha} = 1$ at the exit and then continues to accelerate and expand further as it moves away from the nozzle. It becomes 'over-expanded' since it does not 'know' about P_b and so must be recompressed by a series of shocks. The Mach disk perpendicular to the flow occurs at a characteristic distance from the nozzle and marks a transition from supersonic flow back to subsonic flow. An experimentally derived correlation for the distance from the nozzle to the Mach disk in nozzle units independent from the gas specific heat, is given by [28]

$$\frac{x_M}{d} = 0.67 \left(\frac{P_0}{P_b}\right)^{1/2} \tag{4.15}$$

The barrel shock extends from the nozzle to the outer rim of the Mach disk and forms a boundary between the outside region of background pressure and the zone of silence. The zone of silence is so named because information about conditions outside cannot propagate into it. Between the barrel shock and the jet boundary is a complicated region of viscous, heat conducting, and nonisentropic flow.

In order to avoid scattering and severe attenuation by the shocks, it is necessary to extract a beam from the zone of silence before it encounters the Mach disk. This cannot be done simply by placing an aperture in the zone of silence to select the beam, because the presence of the aperture plate will both set up complex shock waves across the aperture, and reflect off-axis molecules back into the beam causing further scattering. The most common solution is to use a skimmer, a truncated cone with a very sharp leading edge that allows gas to pass through the centre relatively undisturbed, while off axis molecules hit the side of the cone and are deflected away from the axis. Then the flow from the nozzle is considerably simplified and can be treated as a free-jet expansion.

Given that the expansion is supersonic, that is $P_0/P_b > G$, then the gas with a



Figure 4.2: Nozzle with a free-jet expansion through a skimmer.



Figure 4.3: Centre-line Mach number dependence on γ , axisymmetric expansion. From "Atom, Molecule, and Cluster Beams" by Hans Pauly, copyright Springer Science.

molecular weight W exits from the nozzle at a temperature T_0 and pressure of P_0/G , independent of the background pressure, and continues to expand in one-dimensional isentropic flow with negligible heat exchange. Based on these assumptions, an in depth description of the continuum fluid mechanics treatment used to model the expansion has been given by Miller [28], in which Mach number M_{α} can be calculated as a function of position relative to the nozzle and to fit analytical forms to the results as shown in Figure 4.3. We can express all the thermodynamic quantities by using only two parameters: (i) γ the property of the fluid species, and (ii) M_{α} the property of the flow field, as follows:

$$\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2}M_{\alpha}^2\right)^{-1}$$
(4.16)

$$w = M_{\alpha} \sqrt{\gamma \frac{RT_0}{M_{\alpha}}} \left(1 + \frac{\gamma - 1}{2} M_{\alpha}^2 \right)$$

$$(4.17)$$

$$\frac{P}{P_0} = \left(1 + \frac{\gamma - 1}{2}M_{\alpha}^2\right)^{-\gamma/(\gamma - 1)}$$
(4.18)

Figure 4.4 shows how in the initial part of the velocity expansion V increases rapidly to reach 98% of the terminal velocity V_{∞} within the first several nozzle diameters. The temperature though decreases slower, and as the expansion continues and



Figure 4.4: Free jet centre-line properties versus distance in source diameters; $\gamma = 5/3$; temperature *T*, density *n*. From "Atom, Molecule, and Cluster Beams" by Hans Pauly, copyright Springer Science.

the collision frequency drops there comes a point at which there are not enough collisions to maintain equilibrium between the various energy modes of the beam. From here the continuum fluid mechanics description breaks down and the beam properties become frozen. For example, beyond this point, the translational temperature of the molecules motion perpendicular to the beam will be different to that parallel to the beam. Although strictly the transition region is gradual, a useful approximation is to consider a *quitting surface* (or sudden freeze), a hypothetical surface that separates the continuum isentropic region from the free molecular collisionless region [25].

The number of two-body collisions dZ_2 per unit time, which is experienced by a single molecule during the time dt, can be approximated by

$$dZ_2 = n(x)\bar{\sigma}_{eff}\bar{v}(x)dt \tag{4.19}$$

where $\bar{\sigma}_{eff}$ is the mean effective cross section, \bar{v} is the mean velocity of the molecules in the gas at number density n, that are functions of the distance x from the nozzle. In the case of three-body collision, where a pair of molecules must be within a distance r defined as the collision diameter when a third molecule strikes one of them. We can derive the number of collisions by considering the possibility of the third molecule striking the pair which is $r/\bar{\Lambda}$ where the mean free path $\bar{\Lambda}$ is the mean distance between two collisions.

$$dZ_3 = \frac{r}{\bar{\Lambda}} dZ_2 \tag{4.20}$$

The number of collisions which a molecule at a distance x is expected to experience during the rest of expansion is an indication for the clustering process. The formation of clusters requires three-body collisions because of the conservation of momentum and energy. Figures 4.5 and 4.6 are the curves for the number two-body and threebody collisions respectively versus the reduced distance x/d from the nozzle. An example of Argon (Ar) expansion have been used to obtain estimations on two-body and three-body collisions versus distance with the following characteristics for a planar or axisymmetric expansion: $T_0 = 300K$, $P_0 = 5000torr$, $d = 2 \times 10^{-3}cm$ with two different cross-section models, either the hard-sphere model or the Lennard-Jones model [25].

The freezing condition is requiring $Z_2 \approx 10$ collisions and Fig. 4.5(a) shows that it would occur at a distance $x/d \approx 11$ for the Lennard-Jones model and at $x/d \approx 3$ for the hard sphere model, with both of them in an axisymmetric expansion $\gamma = 5/3$. Figure 4.5(b) shows that the quitting would occur at a reduced distance x/d = 3 in the axisymmetric expansion, but it would remain in equilibrium to larger distances in the ideal planar expansion. Which means that the position of the quitting surface



Figure 4.5: (a) Number of two-body collisions $Z_2(x/d)$ remaining in the expansion versus the reduced distance x/d in an axisymmetric expansion $\gamma = 5/3$, calculated for two different collisional cross-sections, for the hard sphere model (1) and for the Lennard-Jones model (2). (b) Number of two-body collisions remaining in the expansion ($\gamma = 5/3$) for a planar (1) and an axisymmetric expansion (2) for the hard sphere model. From "Atom, Molecule, and Cluster Beams" by Hans Pauly, copyright Springer Science.



Figure 4.6: Three-body collisions remaining in the expansion for a planar (1) and an axisymmetric (2) expansion, calculated for $\gamma = 5/3$. From "Atom, Molecule, and Cluster Beams" by Hans Pauly, copyright Springer Science.

depends on the process considered. From Fig. 4.6, we may expect little clustering in the axisymmetric expansion, but in the ideal planar expansion clustering occurs quite easily from the point $x/d \approx 8$.

4-2.1 Velocity Distribution in Nozzle Beams

According to the kinetic theory of gases, the macroscopic properties of a gas can be calculated from the velocity distribution function $f(\mathbf{x}, v, t)$. The number of molecules which, at the time t are situated in the volume element dx at x and have velocities lying in the range dv at v is

$$f(\mathbf{x}, v, t)d\mathbf{x}dv \tag{4.21}$$

The most frequently used model for the velocity distribution is an anisotropic Maxwellian function:

$$f(v)dv = n\sqrt{\frac{m}{2\pi kT_{\parallel}}} \left(\frac{m}{2\pi kT_{\perp}}\right) \exp\left(-\frac{m}{2kT_{\parallel}}(v_{\parallel}-w)^2 - \frac{m}{2kT_{\perp}}v_{\perp}^2\right) dv \qquad (4.22)$$

This distribution function, called an *ellipsoidal drifting* velocity distribution, assumes two Gaussian distributions, but with different widths, in the two directions parallel and perpendicular with respect to the molecular beam line. It reduces to the well known Maxwellian distribution function when $T_{\parallel} = T_{\perp}$. The most useful and simple model to describe the anisotropy of the velocity distribution is the sudden freeze model, discussed in the previous subsection. Figure 4.7 illustrates an expansion that follows the sudden freeze model, in which collisions occur only up to the quitting surface and therefore the distribution of parallel velocities does not change, it *freezes*. However, the perpendicular velocities will continue to decrease and as a result the temperature T_{\perp} of the perpendicular velocity distribution decreases with increasing distance, whereas the temperature T_{\parallel} of the parallel velocity distribution is constant beyond the quitting surface.

One of the most important for molecular beam applications is the final velocity distribution which is dependent on the stagnation conditions and the properties of the seeding gas. We can apply the energy equation (Eq. 4.10) and the thermodynamic principles that we described in section 4-1.2 to determine the flow velocities at two different positions of the expansion

$$\frac{w_2^2 - w_1^2}{2} = h_2 - h_1 = \int_{T_2}^{T_1} c_P dT$$

If we assume that the initial position of the flow w_1 is the stagnation chamber in which the flow velocity is negligibly small $w_1 \approx 0$ with stagnation pressure P_0 and stagnation temperature T_0 . The second position denotes any other point along the isentropic flow where $w_2 = w$ then the integration yields the isentropic discharge



Figure 4.7: Schematic diagram of parallel and perpendicular velocity distributions using the sudden freeze model. Beyond the quitting surface (dashed circle) the distribution of perpendicular velocities continues to decrease because of geometric effects, while the distribution of parallel velocities remains unchanged.

speed w as:

$$w = \sqrt{2\frac{RT_0}{M} \left(1 - \frac{T}{T_0}\right) \frac{\gamma}{\gamma - 1}}$$
(4.23)

The discharge speed reaches its maximum value when the final pressure P is zero, that is when the gas expands into vacuum.

$$w_{\infty} = \sqrt{2\frac{RT_0}{M}\frac{\gamma}{\gamma-1}} = v_w \sqrt{\frac{\gamma}{\gamma-1}}$$
(4.24)

where v_w is the most probable Maxwellian speed in the stagnation chamber, which is defined as the speed at which the distribution function $f(\mathbf{v})$ has its maximum.

The speed ratio $S = w/v_w$ is related to the Mach number by:

$$S = \sqrt{\frac{\gamma}{2}} M_a \tag{4.25}$$

and it was found experimentally that the velocity distribution is related to the speed ratio:

$$f(v) \propto \left(\frac{v}{v_w}\right)^{\nu} \left(\exp\left(-\frac{v-w}{v_w}\right)^2\right) = \left(\frac{v}{v_w}\right)^{\nu} \left(\exp\left(-\frac{v}{v_w}-S\right)^2\right)$$
(4.26)

where v_w is the most probable velocity corresponding to the terminal parallel temperature and the exponent ν depends on the detector used to measure the beam intensity [25]. With increasing values of S the velocity distribution function f(v) approximates a Gaussian distribution with halfwidth:

$$\frac{\Delta v}{w} = \frac{2\sqrt{\ln 2}}{S}$$

An example of the physical meaning of S in clustering can be given by considering the expansion with Ar as seeding gas at $T_0 = 300K$ with $P_0 = 1bar$, which returns a flow velocity $w \approx 560m/s$ with a speed ratio around $S \approx 20 - 40$. As for the case of an expansion with He as seeding gas, which has small mass and extremely small binding energy ($\sim 10^{-7}eV$), therefore condensation is not possible even for high stagnation pressure and low stagnation temperature, we have that the speed ratio is quite high $S \geq 500$.

Furthermore, if we insert the Eq. 4.25 into Eq. 4.16 we can relate the translational

temperature to the speed ratio:

$$T = T_0 \left(1 + \frac{\gamma - 1}{\gamma} S^2 \right)^{-1} \tag{4.27}$$

If we consider again an expansion with Ar with stagnation temperature $T_0 = 300K$, $\gamma = 5/3$ and speed ratio S = 20, we will obtain a translational temperature of $T \approx 2K$. Which means that molecules cool down (internal energy relaxation) during the expansion. Figure 4.5 shows that the total number of two-body collisions experienced by a molecule during the expansion is typically of the order 10^2 to 10^4 . Kinetic processes requiring similar number of collisions in order to relax, for example the vibration of diatomic molecules requires 10^4 collisions and subsequently the vibrational states remain unchanged during expansion. By contrast, the vibration of large polyatomic molecules and the rotation of most diatomic molecules require only 10 to 100 collisions to approach equilibrium with the translational degree of freedom. Therefore, these modes exchange energy and cool down during the beginning of the expansion before reaching their terminal state (freezing). The energy exchange is heating the expansion and could lead to the formation of clusters, as we will describe in the next section.



Figure 4.8: A schematic $\log P - \log T$ phase diagram for the adiabatic expansion of a real gas.

4-3 Cluster Formation

Qualitatively, condensation and cluster formation can be described in both a macroscopic and a microscopic picture. The macroscopic description may be explained with the aid of a schematic P-T phase diagram shown in Fig. 4.8. The adiabatic expansion of a real gas starts at a point A with the stagnation conditions P_0 , T_0 and then it expands along the isentrope up to point B, where it crosses the vapor pressure curve $P_v(T)$. P_v is the vapor pressure of a plane liquid surface. The further expansion continues to follow the isentrope into the liquid phase region. Hence, supersaturation occurs until finally, at the onset point C, the gradual formation of clusters leads to a breakdown of the supersaturated state. The expansion curve returns to the equilibrium curve $P_v(T)$ since the expansion is heated by the released condensation energy.

In the microscopic approach, the starting point for condensation is the dimer formation at the beginning of the expansion as well as dimers (and larger aggregates), which may already exist under the equilibrium conditions in the source. The dimers serve as condensation nuclei for further cluster growth. As long as the cluster number density in the expansion is small compared to the monomer number density, clustermonomer collisions occur predominantly and cluster growth results from successive accumulation of monomers. With increasing cluster concentration, cluster-cluster collisions become more and more important.

4-3.1 Pulsed Molecular Beams

Pulsed sources are defined as the sources for which the pulse duration $\delta \tau$ is small compared to the time interval Δt of two successive pulses [29]. They were developed



Figure 4.9: Intensity of the signal as a function of the laser-nozzle time delay.
in the late 1970s to reduce the amount of materials needed for an experiment by lowering the pumping speed of the nozzle. A pulsed nozzle with pulse length $\delta\tau$ and repetion rate f has a reduced pumping speed by a factor $\delta\tau f$, i.e. for $\delta\tau = 100\mu s$ and f = 10Hz the factor is 10^{-3} . In addition they can improve the signal-to-noise ratio because they produce much higher beam intensities at equal pumping speeds.

As for clustering studies, pulsed nozzles are quite suitable because of their gas pulse shape, shown in Fig. 4.9. Due to the opening and closing of the nozzle we have to probe the molecular beam with the laser beam at a proper time. And depending on the lazer-nozzle time delay we can distinguish three different areas with different beam velocity and temperature in the molecular beam. The first area denoted with temperature T_0 in which the nozzle has just opened and the cooling is not so efficient for cluster formation, thus this area is more suitable to study monomer dissociation. The second area denoted with T_1 which is the most dense part of the beam because the cooling is more efficient ($T_1 < T_0$) and is the most suitable for cluster formation. The third area denoted with T_2 , is actually the tail of the gas pulse and here the cooling is not as efficient as before ($T_2 > T_1$).

Pulsed molecular beams can be formed by using an electromagnetic valve which is mounted within the nozzle. To actuate the stopper of the electromagnetic valve



Figure 4.10: Schematic drawing of a Proch and Trickl piezo-electric source. (1) crystal disk, framed in a metal ring (2), (3) plastic nut with fine thread inside for vertical adjustment of the plunger, (4) aluminium nut to fix the plastics screw, (5) Viton gasket, (6) plunger (with slit for screwdriver on top), (7) lock-nut, (8) value seat sealing O-ring, (9) nozzle flange, (10) front plate, (11) holding rod for disk translator (four are welded into the front plate), (12) stainless steel ring supporting the disk translator with O-ring (13), (14) value body with gas inlet pipe (15) and high voltage feedthroughs (16), (17) eight holes on the circumference for assembling screws. From "Atom, Molecule, and Cluster Beams" by Hans Pauly, copyright Springer Science.

there are three different mechanisms that have been developed more than 30 years ago:

- The current-loop mechanism, in which the magnetic repulsion generated by opposing currents in two parallel conductors opens and closes the valve [29].
- Solenoid mechanism, in which a solenoid (coil) actuated by a current pulse and exerts a force on a moveable ferromagnetic core, is known by its commercial name General Valve [30].
- Piezoelectric mechanism, in which the inverse piezoelectric effect of a crystal opens and closes the valve [31].

In our apparatus described in Chapter 3 we are using a modified Proch and Trickl [31] standard piezoelectric transducer (PZT) pulsed valve, Fig. 4.10 shows a cross-sectional schematic of the original Proch and Trickl valve. The main modification is an extended housing attached to the PZT pulsed valve to act as a gas holder so that the piezoelectric disk is not exposed to the corrosive gases [32].

During the last decade, a renewed interest emerged in the production of pulsed atomic and molecular beams with short pulse widths (FHWM < $10\mu s$) and highrepetition rate up to several kHz. The two modern piezo valves are the Piezo-diskactivated plunger developed by Even and coworkers, an optimized magnetically activated plunger valve that can operate at high backing pressures and has been shown to produce pulsed beams with a duration down to about to $10\mu s$ [33, 34] The second design is the Cantilever piezo valve, developed by Janssen and coworkers that they used a parallel poled bimorph of PZT507 piezomaterial with a high piezoelectric charge constant as the cantilever [35].

4-3.2 Scaling Laws for Cluster Formation

From experimental studies done by Hagena and coworkers [24, 26, 27], we know that supersonic expansion generates aggregates of molecules A_N , up to $N = 2, ..., 10^9$ and to obtain a scaling law which describes the influence of the initial expansion conditions on cluster formation, two types of reactions of a cluster consisting of Nconstituents are considered:

- (i) Bimolecular reactions with monomers:
 - 1. Cluster growth:

$$A_{N-K} + A_K \to A_N$$

2. Energy exchange:

$$A_N + A_K \to A_K + A_N$$

3. Sputtering:

$$A_N + A_K \to A_{N-K} + 2A_K$$

- (ii) Unimolecular reactions of spontaneous decay characterized by the cluster lifetime:
 - 1. Cluster decay:

$$A_N \to A_{N-K} + A_K$$

Figure 4.2 shows an illustration of a nozzle with a free-jet expansion and the corresponding initial conditions, the stagnation pressure P_0 , initial temperature T_0 and the nozzle diameter d. One can determine the mean cluster size \bar{N} by using the initial expansion conditions n_0 , T_0 , and d_0 in the following formula:

$$\bar{N} = K \left(\frac{\Gamma^*}{1000}\right)^{\zeta} \tag{4.28}$$

where K = 38.4 and $\zeta = 1.64$ apply for rare gas clusters [36]. The dimensionless parameter Γ^* introduced by Hagena [26] allows to compare various expansions independent of nozzle and gas parameters (Hagena's scaling law):

$$\Gamma^* = \frac{P_0[\text{mbar}] \times d[\mu\text{m}]^{0.85}}{T_0[K]^{2.2875}} K_{ch}$$
(4.29)

where K_{ch} is a characteristic constant of the seeding gas, e.g. $K_{ch} = 1646$ for Ar. The scaling parameter Γ^* can be used also as a classifier for clustering. Hagena in his pioneering investigations, had sorted different experiments based on their respective Γ^* in increasing order. From the results of these experiments he concluded on the following classification of expansions based on Γ^* parameter:

- (i) $\Gamma^* < 200$ no clustering,
- (ii) $200 < \Gamma^* < 1000$ transition from flow without condensation to flow with formation of clusters (N < 100),
- (iii) $\Gamma^* > 1000$ massive condensation, cluster size exceeding 100 atoms per cluster.

Chapter 5

Iodine Monochloride Ultraviolet Dissociation at 235, 250 and 265nm

5-1 Introduction

One of the open questions in chemical dynamics is the difference in reactivity between the ground and the spin-orbit excited states for a given chemical reaction. Heteroatomic dihalogens such as ICl, BrCl, and IBr photochemistry exhibits many curve crossings and avoided crossings in the excited potential curves and they can be premium photolytic sources to be used for studying reactivity between ground and spin-orbit excited states for a given chemical reaction. Therefore, their UV dissociation has attracted significant theoretical and experimental attention.

Iodine monochloride (ICl) absorption exhibits two broad bands peaking at 270nm and 470nm, respectively [37]. And a number of potential energy surfaces contribute to this absorption [38–40]. By following the labelling of Yabushita [40] the main contributors to the visible band absorption form the ICl(X 0 ⁺(I)) ground state are the A 1 (I), B 0 ⁺(II), and C 1 (II) states which correlate to the first channel of $I({}^{2}P_{3/2}) + Cl({}^{2}P_{3/2})$ and the 0 ⁺(III) and 1 (IV) states which correlate to the second channel of $I({}^{2}P_{3/2}) + Cl({}^{2}P_{1/2})$. The first channel products are being derived from the excited state with $\Omega = 0$ (parallel transition) and the second channel from $\Omega = 1$ (perpendicular transition) The four exit channels have threshold energies ranging from $\Delta E = 2.15 eV$ up to $\Delta E = 3.20 eV$:

- (1) $ICl(\nu=0) + h\nu \rightarrow I({}^{2}P_{3/2}) + Cl({}^{2}P_{3/2}) \qquad \Delta E = 2.15 \text{eV},$
- (2) ICl($\nu=0$) + h $\nu \rightarrow I({}^{2}P_{3/2}) + Cl^{*}({}^{2}P_{1/2}) \qquad \Delta E = 2.26 \text{eV},$

- (3) $ICl(\nu=0) + h\nu \rightarrow I^{*}({}^{2}P_{1/2}) + Cl({}^{2}P_{3/2}) \qquad \Delta E = 3.09 \text{eV},$
- (4) $\operatorname{ICl}(\nu=0) + h\nu \rightarrow I^{*}({}^{2}P_{1/2}) + \operatorname{Cl}^{*}({}^{2}P_{1/2}) \qquad \Delta E = 3.20 \text{eV}$

Several groups have explored ICl photochemistry above 480 nm, de Vries et al. report photofragment spectroscopy results in the 480-530nm range [41]. Probing the Cl fragment, they determined that $Cl^*({}^{2}P_{1/2})$ comes from a parallel transition, while $Cl({}^{2}P_{3/2})$ has both parallel and perpendicular contributions, the latter attributed to curve crossing between B and 0 ⁺ states. In contrast to Child and Bernstein [42] they conclude that the A state has minimal contribution to ICl absorption. Zare group, investigated alignment and orientation of Cl photofragments between 490 and 560 nm [43–45] and report photofragment helicity oscillations due to the interference between A and B states [46]. In the UV band, Tonokura et al. [47] studied ICl photolysis and non-adiabatic crossings in the 235 - 248nm range and measured branching ratios of 0.68 for Cl*/Cl and 0.71 for I*/I, with B, 1 (IV) and possibly ${}^{3}\Sigma^{-}$ states involved.

Recently Samartzis and Kitsopoulos [48] have shown from slice imaging experiments following ICl excitation from 400 to 570 nm that the Cl^*/Cl branching ratio increases with dissociation energy from 570 to 490 nm, and this trend reverses from 490 nm down to 400 nm which is in good agreement with previous studies [41]. The anisotropy parameter β for the I + Cl channel follows the same behavior, rising from -0.41 at 570 nm to 1.18 at 490 nm and subsequently dropping to -0.42 at 400 nm, while the I + Cl* channel beta parameter ranges between 1.4 and 0.6, following the I + Cl channel behavior down to 455 nm but exhibiting the opposite trend from 440 to 400 nm. These results are discussed in light of adiabatic curve crossings and the symmetry of the states involved.

5-2 Experiment

The slicing apparatus used in this Chapter has been described in Section 3-4.3. A supersonic molecular beam of ICl seeded in He is formed with the seed gas flowing over solid ICl and the mixture expanded through a home-made piezoelectrically actuated nozzle valve. Because of the low partial pressure of ICl we have used a modified version of the piezo valve shown in Fig. 5.1. The basic valve design is based on original work of Proch and Trickl [31] with a modification similar to other studies [32, 49]. In order to avoid the exposure of the piezo crystal to the corrosive gas, a bypass chamber is installed that is pressure separated from the piezo containing chamber via an reciprocating O-ring seal on the valve plunger shaft. In our setup



Figure 5.1: Piezo valve design for operation with corrosive gases.

we find essentially no degradation in the traditional performance of our pulsed valve using the traditional design [31]. In addition, we have found that the closer the ICl sample lies to the valve orifice, the denser the beam appears in ICl. We thus mount a "Swagelock-Type" TEE, one side of which is caped and loaded with solid ICl.

The pump laser (235nm, 250 nm, and 265 nm) in our experiments is produced by an Nd³⁺ : YAG pumped optical parametric oscillator-amplifier system (Spectra Physics MOPO). Probe laser is the frequency doubled output of an Excimer-pumped (Lambda Physik LPX) dye laser (LPD3000) using the appropriate dye (Rhodamin 610 and Coumarin480 from Exciton and Radiant Dyes). The probe laser transitions used are $Cl({}^{2}P_{3/2}) \rightarrow 4 p^{2}S_{1/2}$ at 234.632 nm, $Cl({}^{2}P_{1/2}) \rightarrow 4 p^{2}P_{1/2}^{0}$ at 235.204 nm, $I({}^{2}P_{3/2}) \rightarrow 6 p^{4}D_{7/2}$ at 304.578 nm, $I({}^{2}P_{1/2}) \rightarrow 6 p^{4}D_{1/2}$ at 304.047 nm (numbers are laser readings).

5-3 Results

5-3.1 Iodine $(I({}^{2}P_{3/2}))$ Photofragment Images

Representative images (235, 250, and 265 nm) of the I-atoms fragment distributions following ICl photolysis, indicative kinetic energy release (KER) and angular distributions are shown in Fig. 5.2. The KER ideally should have only two peaks corresponding to channels (1) and (2) however a series of peaks are observed due to contaminants in the molecular beam. We have previously performed experiments with CH₃Br that could leave traces in the manifold and result in production of IBr. However, we were able to identify all the species involved in the KERs by using known bond dissociation energies which has lead us to the presence of IBr ($D_0 = 1.86eV$) in the source as well as molecular iodine I₂ ($D_0 = 1.59eV$) [50]. The complete assignment of KER peaks are listed at Table 5-3.1, some of the peaks were assign to "one-color" channels where the probe laser also serves as the photolysis.

The kinetic energy of the nascent fragments can be easily deduced by following Eqs. 3.4 and by using the dissociation energy of ICl $(D_0 = 2.15eV)$ [51]. The channels associated with the ground state iodine in the case of 235nm photolysis, for the production of Cl and Cl^{*} are expected at 0.65eV and 0.68eV respectively. Based on our calibration the main peak appears at 0.65eV and as for the second peak we were not able to detect it, even though the energy resolution required $(\Delta E/E \sim 4\%)$ can be easily fulfilled by our apparatus $(\Delta E/E \sim 1.5\%)$ [52]. However, our group has shown in a recent study of ICl in the visible region, hot bands (rotational and even vibrational) hinder the resolution of Cl and Cl^{*} channels [48].

To help resolve the contribution of these two channels we consider spatial anisotropy of the I-atom photofragment and will make the comparison with the respective images of Cl and Cl* in the following subsections. A typical angular distribution for I is shown in Fig. 5.2(c). We fit the angular distribution using the equation $I(\theta) \sim 1 + \beta P_2(\cos \theta)$ described at Section 2-3.2 and the results are shown in Table 5.2. We observe a negative near limiting $\beta \sim -0.9$ value on the low energy side of the absorption (250 and 265 nm) and a slightly reduced value of $\beta = -0.8$ at 235 nm. The near limiting β value suggests that the dissociation most probably takes place on a single excited potential energy surface, i.e., non-adiabatic transitions are insignificant.



Figure 5.2: (a) I-atom photofragment images at three dissociation wavelengths. At 235 nm, the experiment is performed with a single color. (b) Kinetic energy release (KER) distributions obtained by appropriate radial integration of the slice images shown in (a). (c) Angular distributions obtained by appropriate integrating the slice images shown in (a).



Figure 5.3: (a) I*-atom photofragment images, (b) KERs, and (c) angular distributions.



Figure 5.4: (a) Cl-atom photofragment images, (b) KERs, and (c) angular distributions.



Figure 5.5: (a) Cl^{*}-atom photofragment images, (b) KERs, and (c) angular distributions.

	cora assignmento for an	channels.
A	$I + Cl/Cl^*$	(304.5nm)
B_1	$I + Cl/Cl^*$	(265nm)
B_2	$I + Cl/Cl^*$	(250nm)
B_3	$I + Cl/Cl^*$	(235nm)
Ċ	$I + Br^*$	(304.5nm)
D	$I + I^*$	(304.5nm)
Ε	I + Br	(304.5nm)
F_1	I+Br*	(265nm)
F_2	I+Br*	$(250 \mathrm{nm})$
G_1	I+Br	(265nm)
G_2	I+Br	(250nm)
I	$I^* + Cl$	(304.0nm)
J_1	I*+Cl	(265nm)
J_2	I*+Cl	$(250 \mathrm{nm})$
$\overline{J_3}$	I*+Cl	(235nm)
K ₁	I*+Br	(265nm)
K ₂	I*+Br	(250nm)
L	$I^* + I$	(304.0nm)
N ₁	Cl+I*	(265nm)
N_2	Cl+I*	(250nm)
0	Cl+I*	(235nm)
P ₁	Cl+I	(265nm)
P_2	Cl+I	(250nm)
Q	Cl+I	(235nm)
R ₁	Cl^*+I	(265nm)
$ m R_2^-$	Cl*+I	(250nm)
S	Cl*+I	(235nm)

Table 5.1: KER spectra assignments for all channels.

Table 5.2: Anisotropy parameter results.

	β	$SD(\sigma)$
Ι		
235 nm	-0.76	0.05
$250 \mathrm{nm}$	-0.87	0.05
$265 \mathrm{nm}$	-0.88	0.05
I*		
235 nm	1.90	0.15
$250 \mathrm{nm}$	1.65	0.05
$265 \mathrm{nm}$	1.89	0.05
Cl		
$235 \mathrm{nm}$	1.85	0.06
$250 \mathrm{nm}$	1.93	0.06
$265 \mathrm{nm}$	1.71	0.11
Cl*		
235 nm	-0.72	0.05
$250 \mathrm{nm}$	-0.90	0.05
$265 \mathrm{nm}$	-0.99	0.05

5-3.2 Iodine $(I^*({}^{2}P_{1/2}))$ Photofragment Images

Representative images (235, 250, and 265 nm) of the I*-atoms fragment distributions following ICl photolysis, indicative kinetic energy release (KER) and angular distributions are shown in Fig. 5.3. As in the case of I-atoms described above, a whole series of "unexpected" peaks are observed, that are assigned and detailed in Table 5-3.1. Once again being able to distinguish the two channels (Cl/Cl*) is energetically not possible and will be elucidated by considering the angular distributions. Typical angular distribution for I is shown in Fig. 5.3(c), and limiting values are observed as in the case of I-atom photofragments, however, in the opposite positive limit of $\beta = +2$. We observe a $\beta \sim 1.9$ on either side of the absorption minimum and a slightly reduced value 1.65 at the maximum. Once again the near limiting β value suggests that the dissociation most probably takes place on a single PES, and possibly some non-adiabatic transitions manifest themselves near the absorption maximum at 250 nm.

5-3.3 Chlorine $(Cl({}^{2}P_{3/2}))$ Photofragment Images

Representative images (235, 250, and 265 nm) of the Cl-atoms fragment distributions following ICl photolysis, indicative kinetic energy release (KER) and angular distributions are shown in Fig. 5.4. The large S.O. splitting in Iodine atoms ($E_{SO} = 0.94eV$) allows channels (1) and (3) to be clearly resolved. From the KER spectrum shown in Fig. 5.4(b) we are able to extract the I/I* branching ratio for these two channels and find it to be ~ 10% throughout the wavelengths region studied. In addition β values for the I* channel are near limiting (see Table 5.2) at $\beta = -1.9$. The β value for the I channel because of the weak signal yields large error bars, but we can safely conclude however that $\beta > 1$.

5-3.4 Chlorine $(Cl^*({}^{2}P_{1/2}))$ Photofragment Images

Representative images (235, 250, and 265 nm) of the Cl*-atoms fragment distributions following ICl photolysis, indicative kinetic energy release (KER) and angular distributions are shown in Fig. 5.5. From the KER, within the signal to noise we observe no sibling I* production for the Cl* channel. In blowing up the image contrast we do see some "trace-evidence" that cannot be quantified leading us to conclude that the I/(I* + I) ratio for Cl* is ~ 100%. The β values for Cl* reach -0.7 at 235nm and approach the limiting value of -1.0 at lower energies.

5-4 Discussion

While there have been three previous experimental measurements of the ICl photodissociation in the region reported in this thesis [47, 53, 54] all three of them seem to differ not only in the branching ratios of the four possible channels but even in the angular distribution of the products leading to different excited electronic assignments. In Fig. 5.6 we show a schematic of the most recent potential energy surfaces calculated by Yabushita [40]. As mentioned earlier channel (4) than leads to I^{*} + Cl^{*} is essentially not observed, and is probably the single common observation in all studies of ICl in this region [47, 53, 54]. This can be understood in terms of poor Franck-Condon factors in this energy range, between the $X(0^+, 2440)$ and the $V(0^+, 2422$ and 2332) states, where the notation (pqrs) stands for electronic configuration $\sigma^p \pi^q \pi^r \sigma^{*s}$ [40, 47]. In addition the $0^+(V)$ state does not seem to cross with another electronic state, and the large spin-orbit splitting in Iodine sets this state well separated from the other excited electronic states in this region.



Figure 5.6: Schematic drawing of the potential energy surfaces for the states involved in ICl absorption from Yabushita. The vertical dashed lines and the three circles indicted the region accessed in current experiments.

We now consider channel (2), the only remaining channel producing Cl^{*}. Two sets of information are available depending on which photofragment species is being probed. Comparison of the Cl^{*} and I results in Tables 5-3.1 and 5.2 leads to some interesting suggestions/assertions. Comparing the β values we notice that these are nearly identical within the statistical error bars, and though approaching a limiting value of -1, the slight variation might be informative in deciphering these complex dynamics albeit diatomic species. Two factors could possibly reduce the β value: (a) non-prompt dissociation (excited-state lifetime), and (b) multiple electronic states of opposing symmetry involved. Based on the excited state potentials of Fig. 5.6, the excitation energies in the present study are well above any "bound" part of the potentials and the molecule is placed on the repulsive part of the excited states upon absorption of a photolysis photon. In addition the small rotational constant of ICl $(B \sim 0.1 cm^{-1})$ implies slow rotational motion as expected for two heavy atoms such as Cl and I. Hence we see no reason for anything else except prompt dissociation of ICl in this part of the energy spectrum.

Considering the multiple surface scenario we examine the excited potential energy surfaces involved, i.e., the ${}^{3}\Pi_{0^{+}}(2341)$, ${}^{1}\Pi_{1}(2341)$, and ${}^{3}\Sigma_{0^{+}}(2422)$, that according to the calculations [38–40, 47] are the major contributors to the absorption spectrum at the three wavelengths studied in the report. When considering the spin-orbit interaction in these states a series of $\Omega = 0$ and $\Omega = 1$ states result, of which , the states that correlate to the channel $Cl^* + I$ are the $1(IV, !\Pi_1)$ and $0^+(III, ^3\Pi_{0^+})$ states [47]. When the photolysis wavelength is 265 nm, β is essentially limiting so we can safely conclude that the 1(IV) state is the dominate state involved. However, the calculated transition dipole moment strength in this region indicates that transitions to the ${}^{3}\Pi_{0^{+}}$, ${}^{1}\Pi_{1}$, and ${}^{3}\Sigma_{0^{+}}^{-}$ are approximately equivalent, and if anything the ${}^{3}\Pi_{0^{+}}$ shows the strongest propensity. So if the transition is to remain strictly perpendicular $(\beta \sim -1)$, the contributions of the $\Omega = 0$ states must be somehow "eliminated". One possibility is the Avoided Crossing (Av2) at ~ 6.8 Bohr. The Landau-Zener probability is calculated to be $P_{LZ}^{Av2} \sim 91\%$ and this would be a great "sink" of any parallel-transition ($\Omega = 0$ excited state) contribution. The contribution of the $\Omega = 0$ states is greater at shorter wavelengths (see reduced β values in Table 5.2), and we can estimate the contribution of the parallel component in our experimental data using the relation

$$I(\theta) = A[\frac{3}{2}\cos^{2}\theta] + B[\frac{3}{4}\sin^{2}\theta]$$
 (5.1)

where $A = (1 + \beta)/3$ and B = 1 - A

For 235 nm, lowest wavelength studied here, $\beta = -0.7$ so, A = 0.1, and B = 0.9, which essentially means that our observed ratio of the parallel $0^+(III)$ and $0^+(IV)$ to perpendicular 1(IV) contribution to the I+Cl* channel is

$$\frac{(I+Cl^*)_{\Omega=0}}{(I+Cl^*)_{\Omega=1}} \approx 0.11$$
(5.2)

Based on the potential energy surfaces of Fig. 5.6 we can attempt to predict the experimental ratios determined above. Specifically

$$\frac{(I+Cl^*)_{\Omega=0}}{(I+Cl^*)_{\Omega=1}} = (1-P_{LZ}^{Av2})\frac{(1-P_{LZ}^{Av1})\alpha({}^3\Pi_{0^+}) + P_{LZ}^{Av1}\alpha({}^3\Sigma_{0^+})}{\alpha({}^1\Pi_1)}$$
$$= (1-0.91)\frac{(1-0.8).179 + (0.8).99}{157} = 0.07$$
(5.3)

where P_{LZ}^{Av1} is the Landau-Zener transition probability for the avoided crossing between the ${}^{3}\Pi_{0^{+}}$ and ${}^{3}\Sigma_{0^{+}}^{-}$ at ~ 5.4Bohr, and $\alpha(\Gamma)$ is the transition dipole moment for the respective electronic state [40, 47]. We see that the agreement with the experiment is excellent.

Continuing our "modeling" of the dynamics we can estimate the branching ratio between channels (1) and (3), we have that:

$$\frac{(I+Cl)}{(I^*+Cl)} = \frac{Channel\ (1)}{Channel\ (3)} = \frac{(P_{LZ}^{Av2})[(1-P_{LZ}^{Av1})\alpha(^{3}\Pi_{0^+}) + \alpha(^{3}\Sigma_{0^+}^{-})]}{P_{LZ}^{Av1}\alpha(^{3}\Pi_{0^+}) + (1-P_{LZ}^{Av1})\alpha(^{3}\Sigma_{0^+}^{-})}$$
$$= \frac{0.91 \cdot [(1-0.8) \cdot 179 + (0.8) \cdot 99}{0.8 \cdot 179 + (1-0.8) \cdot 99} = 0.70$$
(5.4)

Analysis of the KER distributions of Cl photofragments at all wavelengths studied yields a propensity ratio for production of

$$\frac{I+Cl}{I^*+Cl} = \frac{Channel (1)}{Channel (3)} \approx 0.10$$
(5.5)

in complete contrast with the theoretical predictions. If we were to "adjust" the theory numbers to fit our experimental observations, we would have $\alpha({}^{3}\Sigma_{0^{+}})$ reduced by a factor of five (20 instead of 99), and the $P_{LZ}^{Av1} \sim 0.9$ (instead of 0.8) and $P_{LZ}^{Av2} \sim 0.7$ (instead of 0.9). The major deviation appears to be the contribution of the ${}^{3}\Sigma_{0^{+}}$ to the spectrum, as the curve- crossing probabilities are not that different from what theory predicts.

5-5 Conclusion

We have studied the photodissociation dynamics of ICl in the UV region between 235 and 265 nm. The spectrum in this region is dominated (~ 95%) by transitions to the ${}^{3}\Pi_{0^{+}}$, ${}^{1}\Pi_{1}$, while the ${}^{3}\Sigma_{0^{+}}^{-}$ excited state contributes only about 5% to the overall spectrum. The I* + Cl* channel is not active in this region while the branching ratios of the remaining 3 channels are estimated as follows:

$$\frac{I+Cl}{I^*+Cl} = \frac{Channel (1)}{Channel (3)} \approx 0.10$$
(5.6)

$$\frac{I+Cl}{I+Cl^*} = \frac{Channel \ (1)}{Channel \ (2)} \ge 0.10 \tag{5.7}$$

$$\frac{I^* + Cl}{I + Cl^*} = \frac{Channel (3)}{Channel (2)} \approx 1$$
(5.8)

In other words the photolysis of the ICl in this region produces about equal amounts of Cl and Cl^{*}, with distinct kinetic energies, and distinct distributions in space, suggesting that ICl could potentially be used as a suitable precursor for studying the relative reactivity of Cl and Cl^{*}.

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Chapter 6

Driving photochemistry by clustering: The ICl···Xe case

6-1 Introduction

Understanding the photochemistry at the molecular level in the bulk requires an answer to the question: *How does photodissociation change with solvation from the individual molecule to the corresponding bulk?* Photodissociation studies in clusters are a viable approach to tackle this problem. In this respect, clustering of molecules with xenon atoms can provide a valuable insight: Xe as the rare gas atom serves as an archetype of chemically non-reactive solvent, yet its interaction can be strong enough to cause electronic effects. In addition, due to its high mass it tends to cluster easily with molecules in supersonic expansions.

Imaging techniques are well suited to study the dissociation dynamics of various atomic and molecular clusters because the photofragment images enclose the complete information about the kinetic energy and angular distributions of the nascent photofragments. Until now the application of imaging techniques to cluster studies has been very limited and related mostly with photodissociation of dimers such as $(CH_3I)_2$ [56, 57], $(ICN)_2$ [58], $(HI)_2$ [59] and pyrrole-Xe [60]. Recently, the photodissociation of hydrogen bromide (HBr) in various large rare gas clusters $HBr \cdots Rg_n$ with tens to hundreds rare gas atoms of either Argon (Ar) or Xenon (Xe) have been studied with VMI paving the way for more imaging studies in large cluster dissociation [61].

Recent theoretical and experimental work on photolysis of pyrrole (Py) with the use of slice imaging, found drastic changes in photochemical behavior of pyrrole when seeded in Xe [60, 62]. The formation of Py-Xe clusters essentially "quenches" the N-H bond breaking for excitation wavelengths longer than 240 nm. This was explained [62] by qualitative altering of the shape of the excited state potential curve in the cluster. More recently, we have observed the influence of Xe clustering on HBr molecule [61]. While in the pyrrole case, the electronic interaction of pyrrole molecule with a single Xe atom explained the experimental results, in the case of HBr it was the *mechanistic effects of caging, delayed cage exit, and direct exit* [63] that were implemented to explain the HBr molecule photodissociation in large Xe-clusters.

To understand the interplay between electronic and mechanistic effects of molecule-Xe clustering, we selected to study the effects of Xe on the photochemistry of ICl. The ICl···Xe system is closer to HBr···Xe case as a diatomic is also involved, so the mechanistic effects proposed for HBr···Xe might also apply. On the other hand, heteroatomic dihalogen molecules like ICl exhibit significant electronic interaction effects such as predissociation, curve crossings, and avoided crossings in the excited state potential curves [37, 40, 42], which might be affected by clustering with Xe.

In Chapter 5 we discussed the photodissociation of ICl in UV region and presented the results at three distinct wavelengths 235 nm, 250 nm, and 265 nm, covering essentially the half width of the absorption spectrum in this region. The results show an almost exclusive production of Cl^{*} with ground state iodine atoms, while the opposite is true for Cl, i.e., the concomitant production of I^{*}. In accordance with all previous studies of ICl in this region, [40, 47, 53, 54] we do not observe the channel leading to I^{*} + Cl^{*} production.

In the following sections, slice imaging results will be presented and discussed from the 235 nm photolysis of ICl seeded in Xe and He. Following photolysis in Xe, Cl, and Cl^{*} photofragment energy distributions become broader and appear at 0.1-0.15 eV higher kinetic energy than for the photolysis in He. For the I and I^{*} fragment distributions, the change is more dramatic: the sharp rings at 0.65 eV (I+Cl^{*} channel) and 0.47 eV (I^{*}+Cl channel) of He photolysis are replaced in Xe with broad distributions extending from 0 all the way to 2.5 eV.

6-2 Experiment

The slicing apparatus used in this Chapter has been described in Section 3-4.3. A supersonic molecular beam of ICl seeded in He or Xe (1100 mbar total backing pressure) is formed with the seed gas flowing over solid ICl at room temperature. This way we generate ICl-Xe and ICl-He mixtures with ICl concentration < 4%. For the

ICl-Xe beam, the nozzle-laser pulse delay is adjusted so that the laser photons excite the species at the peak of the molecular beam velocity distribution, where the strong clustering regime prevails [61]. For the ICl-He beam, the nozzle-laser delay is adjusted so that the laser excites the species arriving at the interaction region $40 - 50\mu s$ earlier than the peak of the molecular beam velocity distribution, thus, exciting only isolated ICl molecules.

The Cl and Cl^{*} photofragment images are recorded in a one-color experiment where one photon is used to dissociate the ICl molecule followed by (2+1) REMPI of the chlorine photofragment within the same laser pulse. The laser beam is generated by a Nd³⁺:YAG pumping a master oscillator power oscillator system (Spectra Physics MOPO). The probe laser transitions used for the detection of Cl and Cl^{*} photofragments are Cl(²P_{3/2}) $\rightarrow \rightarrow 4p(^{2}D_{3/2}^{0})$ at 235.326 nm and Cl^{*}(²P_{1/2}) $\rightarrow \rightarrow 4p(^{2}S_{1/2}^{0})$ at 235.195 nm (wavelengths corrected for laser drift).

The I and I* photofragment images are obtained in a two-color experiment following the photolysis of ICl at 235 nm and (2+1) REMPI of the photofragments, where the laser pulses are separated in time by about 10 ns. The probe laser beam is the frequency doubled output of an excimer-pumped (Lambda Physik LPX, operating with XeCl) dye laser (LPD3000) using the appropriate dye (Rhodamin 610). The I and I* photofragments were probed via $I({}^{2}P_{3/2}) \rightarrow 6p({}^{4}D_{7/2})$ at 304.553 nm and $I^{*}({}^{2}P_{1/2}) \rightarrow 6p({}^{4}D_{1/2}^{0})$ transition at 304.024 nm, respectively. Background images are recorded with the lasers on and the molecular beam off and subtracted from the signal images.

6-3 Results

6-3.1 Cl and Cl* Photofragment Images

Slice images of the Cl photofragments when using He and Xe as the carrier gases are shown in Fig. 6.1. In Fig. 6.1(a) as expected, when using He is the carrier gas the image has two sharp rings: the inner one corresponds to the $Cl+I^*$ exit channel and the outer to the Cl+I channel. The two rings were used to calibrate the kinetic energy release (KER) distribution of Cl photofrgaments. In Fig. 6.1(b), obtained with Xe as the carrier gas, we observe two diffuse rings and an intense feature (blob) in the center of the image. This blob is indicative for the formation of clusters and usually appears as a result of caging processes in which the observed fragments lose their kinetic energy in inelastic collisions with the cluster constituents and are detected as



Figure 6.1: Cl-photofragment slice images following the photolysis of ICl at 235.326 nm recorded using (a) He and (c) Xe as the carrier gas. Cl*-atom photofragment slice images following the photolysis of ICl at 235.195 nm recorded using (c) He and (d) Xe as the carrier gas.

near-zero-kinetic- energy fragments [63].

Figure 6.2(a) shows the KER spectra of the Cl photofragments obtained from the images in Fig 6.2 when using for calibration the dissociation energy value of $D_0(ICl) = 2.15eV$ [11]. In the KER spectrum obtained with He, we observe two distinct peaks at 1.71 and 2.45 eV corresponding to the I^{*} and I producing channels, respectively. When seeding in Xe, the KER spectrum differs substantially showing a slower, wide distribution of a statistical character peaking at around 0.1 eV and two high-energy peaks at 1.81 and 2.55 eV, which are substantially broader and faster when compared to the two peaks from ICl photodissociation in He.

Slice images of the Cl^{*} photofragments when using He as the carrier gas (Fig. 6.1(c)) exhibit an intense sharp ring which corresponds to Cl^{*}+I exit channel at 235 nm. A second faint ring (not quite distinguishable in Fig. 6.1(c)) appears at a smaller radius corresponding to a KER of 1.62 eV. Energetically this ring could be assigned to the Cl^{*}+I^{*} channel, however, our previous study [55] has shown that this channel has zero propensity at this excitation wavelength. It is more likely that it is due to Cl+I channel, where the Cl photofragment undergoes non-resonant multiphoton ionization. When using Xe as the carrier gas, the Cl^{*} photofragment image consists of a diffuse ring and an intense central feature, as shown in Fig. 6.1(d). Figure 6.2(b) shows the KER spectra of the Cl^{*} photofragments obtained from the images in Figs. 6.1(c) and 6.1(d). Similar to the case of the Cl photofragments, when using He we observe one peak at 2.36 eV corresponding to the Cl^{*}+I channel, while the Xe KER features a wide distribution peaking at low kinetic energy and a wide high-energy peak at 2.50 eV which is broader and faster compared to the peak from photodissociation in He.

6-3.2 I and I* Photofragment Images

Figures 6.3(a) - (b) show slice images of the $I({}^{2}P_{3/2})$ photofragments when using He and Xe as the carrier gas, respectively. The image obtained with He shows several rings with the outer one being the most intense. Weaker structures in the center of the image are due to impurities in the gas line, however, they do not interfere with our present analysis. A diffuse ring and a central feature (blob) are observed when seeding in Xe.

Figure 6.2(c) shows the KER spectra of the I photofragments obtained from the images in Figs. 6.3(a) and (b). In the KER spectrum in He, we observe an intense peak at 0.65 eV corresponding to the I+Cl* channel at 235 nm, and a weak peak at 0.39 eV due to photolysis at 304.6 nm by the probe laser, while the additional inner



Figure 6.2: KER distributions of $Cl({}^{2}P_{3/2})$, $Cl({}^{2}P_{1/2})$, $I({}^{2}P_{3/2})$, and $I({}^{2}P_{1/2})$ photofragments are shown in panels (a), (b), (c), and (d), respectively. The black and red lines represent KER distributions obtained using He and Xe as the carrier gas, respectively. The red marks indicate the peak position of the fast component: 1.81 and 2.55 eV in the case of $Cl({}^{2}P_{3/2})$, and 2.50 eV in the case of $Cl({}^{2}P_{1/2})$.

rings of Fig. 6.3(a) have no appreciable intensity in the KER spectrum and could be attributed to dissociative ionization of ICl or I_2 impurity. When seeding in Xe, we observe only a broad distribution extending to ~ 2.5 eV, which is significantly higher kinetic energy than that expected for the ICl monomer.

Figures 6.3(c) and (d) show slice images of the $I^{*}({}^{2}P_{1/2})$ photofragments when using He and Xe as the carrier gas, respectively. The image obtained with He shows several sharp rings, which practically disappear in the case of Xe and a central feature, which could be attributed to beam impurities, dissociative ionization, or even I_{2}/ICl cluster formation. In any case, the contribution of this blob to the overall signal is small as seen in Fig. 6.2(d) and does not affect our analysis. Figure 6.2(d) shows the KER spectra of the I* photofragments obtained from the images in Figs. 6.3(c) and (d). In the KER of He as a carrier gas, we have identified the peaks as originating from the I*+Cl and I*+I exit channels of ICl and I_{2} dissociation at 235 nm and 304 nm. When using Xe, we observe a broad distribution that peaks at low but extends to significantly higher (~ 2.5 eV) kinetic energy release than expected for the monomer.



Figure 6.3: I-photofragment slice images following the photolysis of ICl at 235 nm recorded using (a) He and (b) Xe as the carrier gas. The experiment was performed with two colors. I*-photofragment slice images following the photolysis of ICl at 235 nm recorded using (c) He and (d) Xe as the carrier gas.

6-4 Discussion

6-4.1 Cl and Cl* Photofragment Images

The Cl and Cl^{*} photofragment images obtained using He show only sharp rings as observed before [55], due to photodissociation of the ICl monomer. For the Xe expansion, the images have two features: an intense "blob" feature in the middle of the image, and outer rings broader in distribution and higher in energy with respect to their He counterparts. The central feature points to cluster generation as outlined above. The broad distribution in the corresponding KER spectra of both Cl and Cl^{*} decays exponentially up to $\sim 2-2.5eV$ suggesting that the fragments are formed as a result of dissociation of an ensemble of ICl···Xe clusters of different sizes. This part of the Cl and Cl^{*} KER distributions can be well fit with the following function:

$$f(E) = A_1 exp(-B_1 E) \tag{6.1}$$

or with an equivalent expression in the velocity space, as seen in Figure 6.4:

$$f(v) = A_2 v exp(-B_2 v^2)$$
(6.2)





Where E and v are KER and speed of Cl photofragments, while A and B are the fitting coefficients. This statistical distribution fit is typical for fragments generated in a larger cluster, which lose their kinetic energy due to collisions on their way out of the cluster as previously described by Buck and Farnik [61, 63]. Thus, we propose that this part of the distribution can be attributed to formation of large Xe_N clusters with ICl molecule(s) embedded inside. After ICl photodissociation, the fragments undergo delayed cage exit [63]. The Cl atoms interact several times with the surrounding Xe atoms and leave the cluster with lower velocity than in the case of dissociation of ICl monomer, thus, explaining the low kinetic energies observed.

The fast rings are closer to ICl monomer photolysis as indicated by their angular distribution, however, they have increased kinetic energy release, inconsistent with an ICl monomer dissociation. A possible interpretation is the existence of small clusters consisting of several Xe atoms where ICl molecules are attached to the surface. Dissociation of the I-Cl bond in those clusters would leave Xe_n-I fragments behind and could explain the higher kinetic energies of Cl according to

$$Xe_N \cdots I - Cl \to Xe_N \cdots I + Cl$$
 (6.3)

The KERs of Cl photofragments escaping from such clusters of increasing size are calculated based on the formula below:

$$E_{Cl} = (E_{laser} - D_0 - E_{int}) \times \frac{m_{Xe} \times N + m_I}{m_{Xe} \times N + m_I + m_{Cl}}$$
(6.4)

where E_{laser} is the photon energy, D_0 the I-Cl bond energy, E_{int} the energy of internal degrees of freedom (I* excitation), m_X the mass of species X and N the number of Xe atoms in the cluster. As the number N of Xe atoms in the cluster increases, the mass factor to Eq. 6.4 converges to one and the KER of the outgoing Cl photofragments increases, which explains the shift of the peak to higher kinetic energy. To evaluate the contribution of each cluster to the fast peak, we subtracted the exponential part $A_1 exp(-B_1 E)$ accounting for the cage effect from the overall KER distribution. We fit the remainder with one broad Gaussian (peaking at 1.5 eV) accounting for subtraction imperfections and additional Gaussians (10 proved to be sufficient) of common width, each peaking at the energies calculated with Eq. 6.4.

The result is shown in Figure 6.5. The best fit is obtained when assuming a mass distribution with 32% of ICl in the form of free monomer molecules, another 47% of ICl molecules form Xe-ICl clusters and the remaining 21% of ICl molecules from higher order clusters (N = 2 - 9). Note that although individually they have small



Figure 6.5: Gaussian fit to the KER distribution of the Cl-photofragments. In the legend, n denotes the number of Xe atoms in the cluster, the second number the peak position in eV, and the percentage the contribution of each peak (cluster) to the total peak area without counting the residual peak (the broad peak at 1.5 eV).

contributions, the inclusion of higher order clusters is necessary in order to improve the fit quality on the fast side of the peak.

One can note several imperfections in the model: The Xe-I bond energy, which would shift KER lower, was not taken into account. Also, a certain amount of the energy that is available after photodissociation is consumed during the Xe cluster evaporation process. In addition, some energy is deposited in vibrational modes of the $Xe_N \cdots I$ fragment. Finally one could include clusters with additional ICl molecules either inside or on the surface of the cluster. Therefore, the above numbers for cluster distributions are only an approximation, aiming to show that the proposition of photolysis of cluster-surface-bound ICl can actually interpret our fast-peak data. Based on the above discussion, the Cl and Cl* data point to the existence of two cluster types: cage-like clusters where one or more ICl molecules are surrounded by Xe atoms and relatively small clusters with ICl molecule(s) on the surface where I is bound to the Xe atoms of the cluster. High level theoretical calculations should be able to confirm or disprove this conclusion.

An alternative explanation may involve pure ICl clusters of a broad cluster size distribution. In the small clusters, essentially all the molecules reside on the surface and Cl atom can escape directly after the photodissociation without losing its kinetic energy in the collisions with the cluster constituents. This would yield the faster fragments since the Cl departs against the cluster mass analogically to the $\text{ICl} \cdots \text{Xe}_N$ case. Again, the fast peak would be a sum of weighted shifted peaks calculated for $(\text{ICl})_N$, $N = 0, \ldots, \infty$ (the contribution from the very large clusters would decrease and the shifting in energy would be negligible). The statistical distribution would then correspond to the Cl fragments originating from the interior of those $(\text{ICl})_N$ clusters that are large enough so that Cl could undergo the caging.

We consider the $(ICl)_N$ cluster case to be a weaker explanation of our results since it requires building of sufficiently large $(ICl)_N$ clusters, which seems unlikely in view of the relatively low concentration of our ICl vapor in Xe. Calculating the mean Xe_N cluster size using the famous Hagena's formula [26] for our experimental conditions, we obtain $\bar{N} \approx 400$ for pure Xe expansion and assuming full opening of the valve in the middle of the gas pulse. Thus, we propose the more likely alternative to be the generation of xenon clusters with some ICl molecules, leading to mixed $ICl \cdots Xe_N$ or $(ICl)_M \cdots Xe_N$ clusters.

6-4.2 I and I* Photofragment Images

When it comes to I and I^{*} distributions, Figs. 6.3 and 6.2 and comparisons to Cl/Cl^{*} fragments are extremely illuminating. The change in iodine fragment distribution from He to Xe expansion is more drastic than that of chlorine fragments and no rings are clearly visible. In addition, the angular distribution from monomers to clusters changes significantly. This is more evident in the case of $I({}^{2}P_{3/2})$ (Fig. 6.3 panels (a) and (b)), where the perpendicular angular distribution in He becomes parallel in Xe. Both the angular and KER distributions for the Cl and Cl^{*} in Xe expansion are rather similar. Thus, the first conclusion one can draw is that the effect of Xe is more dramatic for iodine fragments, therefore, Xe should interact more with the iodine rather than the chlorine in the ICl.

We shall use the two cluster types (cage-like and ICl- on-surface) proposed earlier for Cl/Cl^{*} data to rationalize the I/I^{*} observations as well. The lack of I/I^{*} fast peaks matching the Cl/Cl^{*} fast peaks at 1.81 eV, 2.55 eV, and 2.5 eV can be explained by the stereodynamics in the case of the clusters with surface-mounted ICl. If the ICl molecule preferably attaches (anchors) to Xe-cluster moiety, exclusively via the I atom, then upon "impulsive" photodissociation, the iodine photofragment would always be directed to and colliding with the Xe cluster, thus, losing kinetic energy. Therefore, no "direct", fast distinct peaks would be observed for iodine photofragments.

The broad iodine KER distribution features can be explained by cage-like clusters. Iodine KER values slower than that expected for the monomer, can be explained by the delayed cage exit and the cage effect similarly to chlorine fragments above. However, distributions in Figs. 6.2(c) and 6.2(d) include I/I* fragments with significantly higher KER than what would correspond to monomer dissociation, reaching 2.5 eV. Such faster-than-expected fragments have been observed and rationalized previously for acetylene in various clusters including Xe-clusters [64, 65]. The faster fragments were generated by multiphoton processes due to the cage effect: acetylene molecule was prevented to dissociate in the cluster and quenched to a vibrationally excited ground electronic state from which it was dissociated by the next photon yielding the fragment with a kinetic energy increased by the vibrational excitation. It is worth noting that essentially the same effect was observed also upon dissociation of HBr in rare gas clusters, where it however resulted in a well resolved additional ring at higher energies in the images [61]. In the present case, caging to vibrationally excited ICl is possible but rather unlikely since it would also yield much faster Cl fragments than those observed.

Another possible scenario would be generation of XeI molecule or Xe_NI cluster upon ICl dissociation in the cluster and subsequent Xe-I dissociation in multiphoton process which would yield the faster I fragments. The formation of the Xe_NI would be consistent with the surface mounted ICl argument above, and the fact that we see no evidence for similar XeCl species generation further favors our suggestion that the ICl preferably anchors to the surface of the Xen cluster almost exclusively via the I-atom.

6-5 Conclusions

We present the dramatic effects that even a noble seed gas like Xe can have on the photochemistry of a relatively simple diatomic molecule like ICl. In ICl photolysis in molecular beam of He and Xe seed gases, we observe broadening of the monomer peaks, which is more severe in the case of I and I^{*} where even angular distributions are changing from perpendicular to parallel. The KER of Cl and Cl^{*} increases in Xe compared to that in He. We explain these observations based on formation of two cluster types: a cage-like type where one or more ICl molecules are embedded in Xe and another type where small clusters of Xe or Xe-ICl cores feature an ICl molecule on the surface.

Although many open questions remain about the actual mechanism of the observed effects, the experimental evidence is solid and well interpreted by the rather qualitative models of cluster dissociation proposed. A more detailed insight into the photodissociation dynamics in the present clusters requires high level theoretical treatment, which goes beyond the present purely experimental paper. Yet one of the contributions of the present work is to stimulate such theory to treat these exciting problems of molecule photochemistry in confined cluster environments. Our present results continue the effort to understand clustering effects on molecular photochemistry. These effects have now been observed in a number of systems extending from diatomic to polyatomic molecules and need additional experimental and theoretical work to be understood in detail.

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Chapter 7

Photodissociation of Methyl Iodide and Methyl Iodide Clusters at 193nm

7-1 Introduction

The plethora of studies on the photodissociation of CH_3I , especially in its first absorption band (A-band), have constituted CH_3I as a prototypical molecule for studying dissociation processes in polyatomic molecules. The diatomic-like breaking of the C-I bond combines the simplicity of unidimensional bond breaking with the complexity of polyatomic molecular dynamics, such as different absorbing states, nona-diabatic crossings, and energy partitioning between electronic, vibrational, and rotational states. The A-band ranges from 220 nm to 350 nm and is characterized by prompt direct dissociation, as indicated by its broad, weak, and diffuse spectrum lying below the lowest Rydberg state [67, 68].

The *B*-band is not so thoroughly studied as the A-band, but it has begun attracting significant attention [69–74]. The origin of the *B*-band stems from the excitation of a lone pair e(5p) electron in the iodine atom to a 6s Rydberg orbital $5 p\pi \rightarrow \sigma$ covering the spectral range from 188 to 205 nm and shows clear vibrational structure. A recent study using high resolution VUV photo-absorption in the 6 - 10.5 eV (207 -118 nm) region has returned more than 200 lines [75]. Its dynamics have been characterized featuring a fast predissociation (lifetime 1.5 ps) due to crossing with repulsive states from the *A*-band [70, 76, 77]. The ArF laser light (193.3 nm) employed here excites the 2_0^2 band of the B state [69, 78]. Two distinct dissociation channels lead to the production of ground state CH_3 with ground state iodine $I({}^{2}P_{3/2})$ and spin-orbit excited iodine $I({}^{2}P_{1/2})$, labeled from now on as I and I*, respectively. A discrepancy concerning the Φ^* quantum yield in the B-band, that is, how much I* is produced, arises from the relevant literature. For excitation at 193 nm, Hess et al. [79] report a $\Phi^* = 0.70 \pm 0.04$, while Continetti et al. [78] and Veen et al. [80] estimate this quantum yield to be close to unity. Gilchrist et al. [69], using two different diode laser methods, obtained two different values: $\Phi^* = 1$ and $\Phi^* = 0.68 \pm 0.04$. More recently, Velocity Map Imaging (VMI) and slice imaging studies found, $\Phi^* = 1$ at 201.2nm [70], $\Phi^* = 1$ at 196.7nm [72] and $\Phi^* = 0.95 \pm 0.01$ at 199.1nm [71].

In this chapter we investigate how the dynamics of CH_3I in the *B*-band are affected by clustering in supersonic expansions when using He and Xe as seeding gases. Recently large clusters such as $HBr \cdots Xe$ [61] and $ICl \cdots Xe$ [66] have been studied using VMI and slice imaging, respectively. Molecules such as HBr and ICl have well-known dissociation dynamics that change dramatically when clustered even with a single Xe atom [61, 66]. In certain cases such as $Py \cdots Xe$, active reaction channels in the bare molecule can be switched OFF, as the clustering introduces significant changes in the excited potential energy surfaces [60]. Previous experimental and theoretical studies on hydrogen halides have shown three main different photodissociation mechanisms for weakly bound clusters where the molecule under study is embedded in the cluster and surrounded by atoms such as Xe or Ar [63, 81, 82]. First, the direct cage exit where the photofragments could escape without interacting inelastically with the surrounding atoms, and their kinetic energy resembles that of the free molecule. The second case is the *delayed cage exit*, where the photofragments are interacting with the surrounding atoms, resulting in significantly lower kinetic energy. The third case is the *cage-effect*, where photofragments are interacting so many times that they are losing all their kinetic energy and are ready for recombination.

Using slice imaging, we have acquired photofragment images of I, I^{*}, and CH₃ ($\nu_2 = 0, 1, 2, 3$) from the photolysis of CH₃I at 193 nm using both helium and xenon as seeding gases. We confirm previous work on the *B*-band dynamics (especially on the absence of the CH₃ + I channel at 193 nm for the states probed) and observed significant changes in the dynamics when clustering in Xe. More specifically, CH₃ fragment distributions for clusters exhibit a parallel character (compared to the perpendicular one of the CH₃ from the CH₃I monomer), they peak at higher KER than the monomer CH₃ fragments, and their KER actually increases with ν_2 quantum number, being 0.5eV higher than the monomer for $\nu_2 = 3$. When probing iodine atoms, no ground state I fragments are observed, while the I^{*} ones span a wide range

of KERs [83, 84].

7-2 Experiment

The slicing apparatus used in this Chapter has been described in Section 3-4.3. A molecular beam (1000 mbar total backing pressure), with a mixture of $CH_3I \sim 2.5\%$ in He or Xe, is used. The mixture is expanded through a homemade piezoelectrically actuated nozzle valve (1mm diameter) [31] and skimmed before it enters the detection chamber, where the ion optics are positioned. After passing through the 2 mm diameter orifice in the repeller electrode, the molecular beam is intersected at right angles by the photolysis and photofragment ionization lasers at the geometric focus position of a single-electrode repeller-grid arrangement [20].

The timing of the dissociation and ionization lasers with respect to the gas pulse was carefully selected during the experiments. Evidence of clustering typically manifests itself though structureless features ("blobs") with small kinetic energy release, that appear at the center of a photofragment image. Even when using helium as seeding gas, $(CH_3I)_N$ clustering is observed when photodissociating in the most dense part of the molecular beam (peak intensity). When so desired, to ensure that only monomers are present, it was necessary to operate in the early part of the molecular beam expansion, where gas density is low and gas cooling not as efficient. On the contrary, when clustering was desired, experiments were performed at the maximum intensity of the molecular beam.

For the slicing experiments reported here, the repeller is pulsed ON (3 kV) at the appropriate time (typically 300 ns) following the photoionization. The photofragments traverse a field-free time-of-flight region and are detected by a position- sensitive detector (dual, imaging-quality MCP array coupled to a phosphor screen). The detector is gated such that the center slice of the photofragment Newton sphere is imaged. The image frame is recorded asynchronously every second (10 laser shots) by a CCD camera, and several thousand frames are averaged to form images. Each final image is appropriately integrated to extract kinetic energy release and the angular distributions of the photofragments. We recorded images with photolysis and ionization laser polarizations parallel to each other and to the imaging detector plane (XX geometry) as well as images where photolysis and ionization laser polarizations are parallel to each other but perpendicular to the imaging detector plane (ZZ geometry). The later are used to "normalize" the XX images for artifacts such as detector inhomogeneities, laser profiles, etc., especially in extracting the angular distributions. The photolysis laser is an excimer laser (Lambda Physik COMPex 110) operating with an ArF mixture giving unpolarized light at 193 nm with a pulse duration of 25 ns. Brewster reflection is used to polarize the laser. The ionization laser is produced by a MOPO (master oscillator power oscillator) system (Spectra Physics MOPO 730D10) pumped by a Nd:YAG laser (Spectra Physics Pro Series 450). The photolysis and photoionization laser pulses (~ 0.5mJ per pulse each) are separated in time by about 10ns, in order to avoid multiphoton effects. The I and I* photofragments were ionized by (2 + 1) REMPI through the $6p^4D_{7/2} \leftarrow (^2P_{3/2})$ at 304.504nm and $6p(^4D_{1/2}^0) \leftarrow$ $\leftarrow (^2P_{1/2})$ at 303.984nm transitions, respectively. The CH₃ photofragments are resonantly detected at the following *Q*-branch transitions (3 p_z $^2A_2'')$: 0_0^0 (333.500nm), 2_1^1 (329.595nm), 2_2^2 (326.162nm), and 2_3^3 (322.859nm). Background images are recorded with the photolysis laser off and subtracted from the signal images.

7-3 Results and Discussion

7-3.1 CH₃ Photofragment Images

Shown in Figure 7.1 are photofragment images of CH_3 ($\nu_2 = 0, 1, 2, 3$) from the photodissociation of CH_3I at 193nm with either helium (top row) or xenon (bottom row) as seeding gases. When seeding in He, three features are observed in each image: two rings and a central blob. The outer ring is assigned to photolysis of the monomer CH_3I by the 193 nm laser, while the second inner ring is assigned to photolysis of CH_3I by the probe laser (333 - 323nm depending on the ν_2 state probed). For $\nu_2 = 3$ we observe no inner ring. The structure-less "blobs" in the center of the image are attributed to $(CH_3I)_N$ clusters. As mentioned earlier, when seeding in helium and using low stagnation pressures (1 atm), we do not expect a significant amount of clustering. However, as the absorption cross section of CH_3I at 193 nm is extremely weak, in order to obtain images with adequate signal-to-noise, the experiments were performed in the densest part of the molecular beam, facilitating $(CH_3I)_N$ cluster formation. Efforts to eliminate experimentally the photolysis contribution of the ionization laser proved unsuccessful, as sufficient photon flux is necessary to ionize via 2 + 1 REMPI, which makes the 1-photon photolysis of CH₃I by the probe laser unavoidable. As shown in Figure 7.2, subtracting this "photolysis" contribution of the probe laser from the image eliminates the central blob, therefore suggesting that the 193 nm absorption of $(CH_3I)_N$ clusters is negligible.

Similarly, in the lower panel of Figure 7.1, while seeding in Xe, a central blob



Figure 7.1: Photofragment images of CH_3 ($\nu_2 = 0, 1, 2, 3$) with either helium (top row) or xenon (bottom row) as seeding gases. Vertical "fringes" observed in some images (usually with very high or very low intensity) are an artifact due to the "interlaced" Photolysis and photoionization laser polarizations are parallel to each other and to the imaging detector plane (XX geometry) mode of operation of our CCD camera (separate reading of odd and even CCD lines)



Figure 7.2: Photofragment images of CH_3 ($\nu_2 = 0, 1, 2, 3$) with the probe laser subtracted with either helium (top row) or xenon (bottom row) as seeding gases.



Figure 7.3: Kinetic energy (KE) distributions of CH_3 ($\nu_2 = 0, 1, 2, 3$) photofragments with either helium (blue color) or xenon (red color) as seeding gases are shown in panels a - d, respectively.

feature and an outer ring are observed. Images where the probe laser contribution has been subtracted are shown in Figure 7.2. It is evident that only the probe laser contributes to the central blob, and residual "features" around the center of the image arise from incomplete subtraction of the probe laser because of the weak signal. However, in this case, the central blob may be $(CH_3I)_N$ or $(CH_3I)_N \cdots Xe_M$ clusters, as we cannot a priori rule out the existence of mixed clusters of the type $(CH_3I)_N \cdots Xe_M$. In addition, as will be discussed below, assigning the outer ring solely to monomer CH_3I photodissociation is not satisfactory, as it exhibits drastic differences from the He data images.

Figures 7.3 and Fig. 7.4 show the corresponding KERs for the photofragment images of Figures 7.1 and 7.2, respectively. Tick marks indicate the predicted KER positions of CH_3 (ν_2) fragments using the relation:

$$KER_{CH_3} = \frac{m_I}{m_{CH_3I}} (h\nu - D_0 + E_{int}(CH_3I) - E_{SO})$$
(7.1)

where m_I is the mass of iodine, $h\nu$ is the photon energy corresponding to the photolysis or ionization laser, $E_{iint}(CH_3I)$ is the internal energy of CH₃I (negligible), $D_0 = 2.41 \text{eV}$ [67] is the dissociation energy of the parent molecule CH₃I, and $E_{SO} = 0.94 \text{eV}$ [50] is the spin-orbit energy in iodine.

In the CH₃ KER distributions, for He expansions, the low energy $(CH_3I)_N$ cluster signal is observed to be stronger for the $\nu_2 = 1$ and $\nu_2 = 2$ compared to the $\nu_2 = 0$ and $\nu_2 = 3$, while in all cases the monomer peak (2.5 - 3.5 eV) from the 193 nm photolysis dominates. This trend changes in the case of Xe, where the 2.5 - 3.5 eV peak is larger than the low energy cluster blob for $\nu_2 = 1$ and $\nu_2 = 3$ but smaller for $\nu_2 = 0$ and $\nu_2 = 2$. What is common in both Xe and He is that the central blob contribution is mainly from the probe laser, while the 193 nm photolysis gives rise to the faster, outer peak. The discussion on these two features will be done separately, in order to emphasize their differences.

Probe Laser (323 - 333.5nm) Dynamics

Our observations indicate that the blob features in both He and Xe expansions have identical behavior, leading us to believe that this is due either to identical clusters or to clusters that follow similar photodissociation dynamics. Previous work on HBr, and ICl clustering, concluded that such features originate from a cluster *cage-effect* [61, 66]. According to this model [63], molecular photodissociation occurs inside a large cluster, and in the case of CH_3I , the nascent CH_3 undergoes a large number of collisions with cluster elements, thus losing almost all of its kinetic energy. The methyl radical photofragment can either recombine with iodine to form again CH_3I with higher internal energy than the parent or remain caged with near zero kinetic energy that results in the central blob in our images.

Typical KERs resulting from a classical cage-effect or delayed-cage-exit are peaking at or very close to 0 eV [61, 63, 66], as in the case of $(CH_3I)_N$ seeded with He in Figures 7.3b-d (blue lines). However, the slow KER component for Xe as seeding gas (red line) corresponding to a probe laser (333 - 323 nm) is peaking at significantly higher energies, up to 1.2 eV for $\nu_2 = 1$. Besides the mechanistic effects of the cage-effect, one could additionally suggest a number of different scenarios, such as statistical decay of the molecule inside the cluster where the direct dissociation of the molecule is hindered due to clustering with Xe atoms and could result in a hot CH_3I with higher dissociation energy. Subsequently, the cluster evaporates and the molecule decays with the KE of the nascent fragments to follow a statistical distribution. This assumption is supported by the Maxwellian-like shape of the slow
193nm channel	Helium	Xenon
$CH_3(\nu_2=0)$	$\beta = -0.37 \pm 0.02$	$\beta = -0.30 \pm 0.03$
$CH_3(\nu_2 = 1)$	$\beta = -0.36 \pm 0.02$	$\beta = -0.10 \pm 0.02$
$CH_3(\nu_2 = 2)$	$\beta = -0.53 \pm 0.03$	$\beta = 0.10 \pm 0.02$
$CH_3(\nu_2 = 3)$	$\beta = -0.32 \pm 0.02$	$\beta = 0.13 \pm 0.01$
$I({}^{2}P_{1/2})$	$\beta = -0.67 \pm 0.01$	$\beta = 0.09 \pm 0.04$

Table 7.1: Anisotropy parameter β obtained by fitting angular distributions from the images shown in Figs. 7.1 and. 7.6.

component for Figure 7.3c and 7.3d.

Pump Laser (193nm) Dynamics

The KER spectra for the 193 nm photolysis are shown in Figure 7.4. When seeding in Xe, the peak appears to broaden and to shift toward higher KER with respect to the He expansion, especially as the ν_2 excitation increases. This indicates that this peak in the case of Xe expansion either (a) corresponds to extremely different CH_3I internal energy or (b) must contain a contribution from clusters of the type $(CH_3I)_N \cdots Xe_M$. We expect expansion using Xe to lead to more efficient cooling, so we favor the second explanation. The energy shift in the KER to higher energy would mean weakening of the C - I bond because of the clustering, while in addition the heavier mass of the parent cluster will impart more kinetic energy in the light methyl radical, assuming an impulsive dissociation and that the internal rotational energy partitioning in daughter radicals remains about the same. This later assumption is contradicted by the broadening of Xe peak, which would mean that the CH_3 radical product is rotationally hotter. Alternatively, this increased width could simply be the fact that, unlike the photodissociation of the monomer CH_3I , where the sibling I-atom fragment can only have electronic energy,

$$CH_3I \longrightarrow CH_3(\nu_2) + I(e)$$
 (7.2)

in the case of the clusters, the extra degrees of freedom in the cluster fragment allow for a wider range of KER even when a single ν_2 quantum state of the CH₃ is probed, that is,

$$(CH_3I)_N \cdots Xe_M \longrightarrow CH_3(\nu_2) + (CH_3I)_{N-1} \cdots Xe_MI(\nu, J, e)$$
 (7.3)

Further support of this assignment stems from the angular distribution of this



Figure 7.4: Kinetic energy (KE) distributions of CH_3 ($\nu_2 = 0, 1, 2, 3$) photofragments corresponding only to a photolysis laser (193 nm) with either helium (blue color) or xenon (red color) as seeding gases are shown in panels a-d, respectively.

peak, where the anisotropy parameter (Table 7.1) is increased from -0.4 in the case of $CH_3I(\nu_2 = 1)/He$ to -0.1 in the Xe expansion, indicating that species other than CH_3I monomer are contributing to this feature. The effect just described for $\nu_2 = 1$ becomes even more drastic for $\nu_2 = 2$ and $\nu_2 = 3$, but what is even more remarkable for these vibrational states is that the angular distributions for the Xe peak become positive, $\beta \approx +0.1$, from the initial value, -0.4, in the CH_3I monomer. The "four-leaf clover" shape observed in the $\nu_2 = 1$ XX image (Figure 7.2) distribution disappeared when normalized with the $\nu_2 = 1$ ZZ image distribution. This was confirmed by fitting the distributions with an expanded set ($\beta_2, \beta_4, \beta_6$) of β parameters which showed all β_4, β_6 values to be essentially zero, as shown in Fig. 7.5.

Angular distribution expresses the change in electronic state symmetry between ground and excited states, and in the cases where photodissociation is not prompt, the lifetime of the excited state "reduces" the anisotropy parameter. However, in the long lifetime limit, a maximum reduction by a factor of 4 is expected [85]. A change in sign of the β anisotropy parameter signifies completely different dynamics or electronic



Figure 7.5: Angular distributions obtained by normalizing the photofragment image of $CH_3(\nu = 2)$ XX geometry with its corresponding ZZ geometry

states; that is, the fast peak in the Xe case must be primarily photodissociation of clusters. The drastic changes of β could be explained by considering the dissociation process on some excited potential energy surfaces, but the process would have to be of parallel character, as suggested by Figures 7.1 and Fig. 7.2. This scenario also justifies the existence of mixed species in the molecular beam.

he 193 nm excitation clearly shows different dynamics than the 333 nm excitation (probe laser/central blob), so a different mechanism must be used to explain this feature. In a recent study on ICl···Xe_M clusters [66], one such alternative approach was shown to explain similar behavior. In particular, if we assume that CH₃I molecules lie on the surface of a cluster $(CH_3I)_N \cdots Xe_M$, the slightly higher KE of the methyl photofragments from such surface bound CH₃I molecules could be understood from Eq 7.2, where the mass scale factor is different in the case of the cluster, given by $m_{(CH_3I)_{N-1}Xe_MI}/m_{(CH_3I)_NXe_M}$. However, in the case of the monomer this mass ratio is already 0.90, so even in the extreme limit of very large clusters, with all other factors remaining the same, a maximum shift of only 10% is expected. Hence, this could explain small shifts in the KER, such as those in $\nu_2 = 1$ or $\nu_2 = 2$, but not the difference of 0.5 eV observed in the case of $\nu_2 = 3$.

To explain the high KER shift of 0.5 eV in $CH_3(\nu_2 = 3)/Xe$, one could suggest a multiphoton mechanism as in the case of acetylene [64], where the molecule is excited by the first photon but quenches to a vibrationally excited level of the ground electronic state and is dissociated by a second photon. These studies showed that the absorption of the second photon by the decaying molecule is possible even at low photon fluxes where only single-photon processes are observed for the isolated molecule.

Total caging of the photofragments and recombination back to the parent molecule with higher internal energy, as in the case of $\text{HBr} \cdots \text{Xe}_M$ [61], is not likely because there are no extra rings as like in the HBr case. More theoretical treatment is needed to have a complete understanding of the clustering mechanism of CH_3I with rare gases such as Xe, and several considerations have to be made, such as the vibrationally dependence and the different dynamics of each absorption band of CH_3I .

7-3.2 I and I* Photofragment Images

Recently a femtosecond slice imaging study has shown evidence of the channel $CH_3 + I$ at 199.11nm [71]. Figure 7.6, shows the photofragment images of ground state I and spin-orbit-excited I* atoms we obtained in expansions of He or Xe, and the corresponding KER distributions are plotted in Figure 7.7. When probing I-atoms in He, our results clearly indicate that the 193 nm photolysis laser has a negligible contribution, even when we perform the experiment at the peak of the molecular beam pulse where cluster contributions from $(CH_3I)_N$ become evident (Figure 7.6, top left). In Figure 7.7, we assign the 0.2 eV peak to the "monomer" photodissociation at 304.5 nm:

$$CH_3I \longrightarrow CH_3(\nu, J) + I$$
 (7.4)

On the contrary, when probing I* in He, two rings are present (Figure 7.6, top right), with the outer one attributed to the 193 nm and the inner one to the 304 nm photolysis of CH₃I. Figure 7.7(b) (blue line) indicates that the dominant feature in the KER is the 193 nm photolysis. The lack of $(CH_3I)_N$ clustering in the He signal is due to the fact that the strength of the I* REMPI line allows image recording at very early beam times where no clusters are yet formed. In the Xe expansion, the I* image shows essentially a center-peaking blob; however, the KER distribution features a slow and fast part in that blob consistent with I* production at 304 and 193 nm photolysis, respectively. It is safe to conclude that the yield ratio I*/(I + I*) is essentially unity at 193 nm; that is, when photodissociating CH₃I at 193 nm using a nanosecond laser no ground state iodine atoms are generated.

When probing CH_3 , we attributed the KER shift to the surface bound clusters.



Figure 7.6: I (left column) and I* (right column) photofragment images with either helium (top row) or xenon (bottom row) as seeding gases. Vertical "fringes" observed in some images (usually with very high or very low intensity) are artifacts due to the "interlaced" mode of operation of our CCD camera (separate reading of odd and even CCD lines).

The fact that this is absent when probing the large iodine atoms (either ground or spin-orbit excited) is reminiscent of the behavior reported in our previous study on $ICl \cdots Xe_M$ clusters [66]. In order to explain this behavior, we assumed that the surface molecule, in this case CH_3I , is preferentially attached to the cluster moiety via the large iodine atom. In such a geometry, following prompt (impulsive) photodissociation, the I-atom photofragment would collide with the cluster main body and, hence, the probability of prompt dissociation would be eliminated. Hence, we are seeing a very similar behavior in the case of the pseudodiatomic CH_3I and the ICl molecule when forming clusters in Xe mediated expansions.

7-4 Conclusions

Our results indicate that photodissociation of CH_3I at 193 nm yields exclusively Iatoms in their excited spin orbit state I^{*}. When expanding in Xe, clusters are formed, which show significantly different dynamics than those of the isolated monomer. Our analysis indicates two types of clusters: one indicating cage dynamics, where the precursor CH_3I molecule is embedded in a large cluster of Xe_M and $(CH_3I)_N$, and a second where the precursor is mounted on the surface of the cluster. In addition, the KER spectra provide evidence that the surface mounted methyl iodide anchors to the cluster moiety via the iodine atom.

This chapter has been published in The Journal of Physical Chemistry C [86].



Figure 7.7: Kinetic energy (KE) distributions of I and I^{*} photofragments with either helium (blue color) or xenon (red color) as seeding gases are shown in panels a and b, respectively.

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