

Chapter 1

Introduction

1.1 Background

Since the discovery of the atom and its structure, consisting of a nucleus containing smaller particles (neutrons and protons) and electrons which surround the nucleus, scientists have been studying the electronic structure of atoms and molecules. More specifically, the field of quantum mechanics has attempted to understand electronic structure, among other things, and how it relates to the chemical bonds that are formed between atoms. Fundamentally, understanding the nature of chemical bonding is important for the advancement of science. Many practical uses stemming from our knowledge of chemical bonds exist as well in all fields of science, from understanding the gene sequences in DNA to controlling chemical reactions in the atmosphere that cause pollution.

To get at the fundamental electronic structure underlying bonding in molecules, scientists have long relied on the experimental technique of photoelectron spectroscopy. Photons are used to eject electrons from molecules or atoms (termed 'ionization'), and the energy of the electrons is used to infer orbital energies, or discrete energy levels of the electrons in a molecule. When atoms come together to form molecules, the electrons in the outer shell (or valence orbitals) are primarily responsible for the formation of chemical bonds. By ejecting these electrons via photoelectron spectroscopy, it is possible to better understand how atomic orbitals become molecular orbitals. Fig. 1.1 is a simplistic picture of two atoms with one specific orbital energy coming together to form two molecular orbitals. In a simplified view, the electrons in these outer

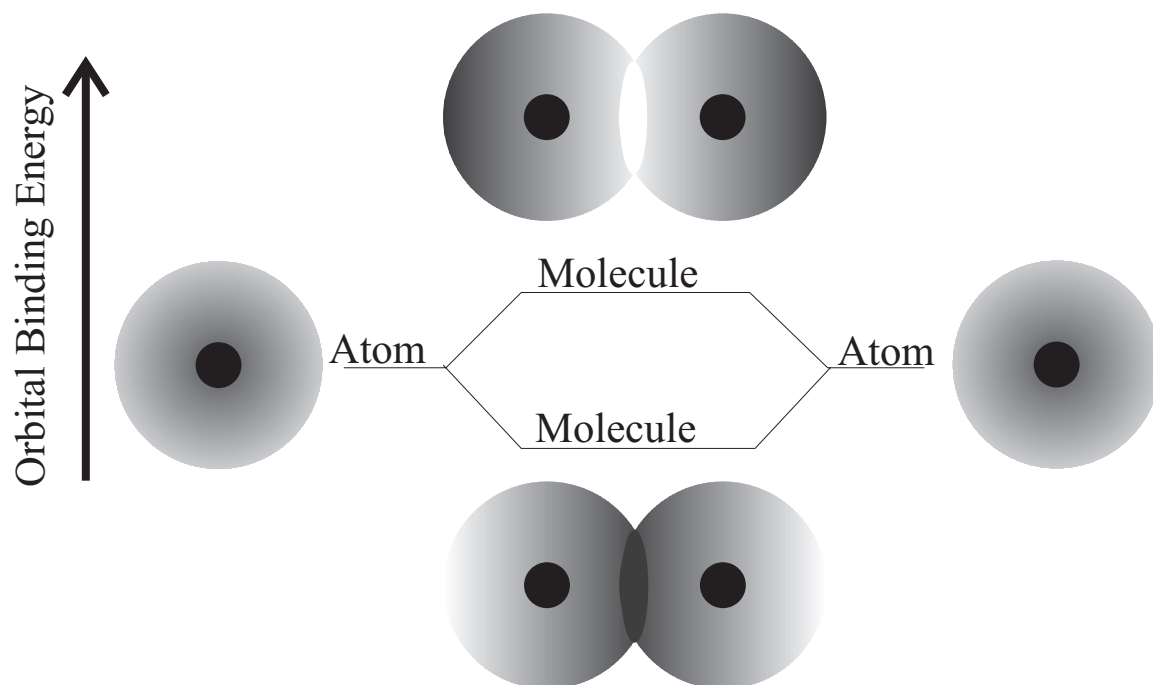


Figure 1.1: A simple molecular orbital picture demonstrating two atoms coming together to form two molecular orbitals.

molecular orbitals now share the space around the two nuclei. In a multi- electron system, a series of molecular orbitals are formed, from the core orbitals (the electrons close to the nucleus) to the valence orbitals (the electrons furthest away from the nucleus and largely responsible for bonding).

In photoelectron spectroscopy, when a photon with a particular energy interacts with a molecule, an electron is ejected, as is demonstrated in Fig. 1.2. To eject a valence or outer electron with a small binding energy, a lower energy photon is sufficient. To eject a core or inner electron with a large binding energy, a higher energy photon is needed. This leads to the conservation of energy given by the equation:

$$\hbar\nu = E_{pe} + I_i \quad (1.1)$$

where $\hbar\nu$ is the photon energy, E_{pe} is the energy of the ejected photoelectron and I_i is the ionization energy, or binding energy of the orbital i . Equation 1.1 is an approximation resulting from Koopmans' theorem, which states that the ionization energy is equal to the orbital energy of the ejected electron. This neglects the fact that the remaining electrons rearrange their distributions when ionization occurs [1].

There are several ways experimentally to measure the energy of the ionized electron in photoelectron spectroscopy. An electrostatic analyzer utilizes the fact that the energy of the electron is related to its velocity, as is given by the extension of equation 1.1 to:

$$E_{pe} = \frac{1}{2}mv^2, \quad (1.2)$$

where v is the velocity of the electron and m is the mass. The electrostatic analyzer consists of two charged plates bent at an angle. When these plates are held at a certain voltage, the deflection path of the electron depends on its speed, and electrons with different speeds will make it through the analyzer to the detector as the voltages are changed (Fig. 1.3(a)). If the voltages are ramped in a consistent way, a full photoelectron spectrum can be obtained. Another common method of analyzing the energies of photoelectrons is with a time-of-flight tube. Here,

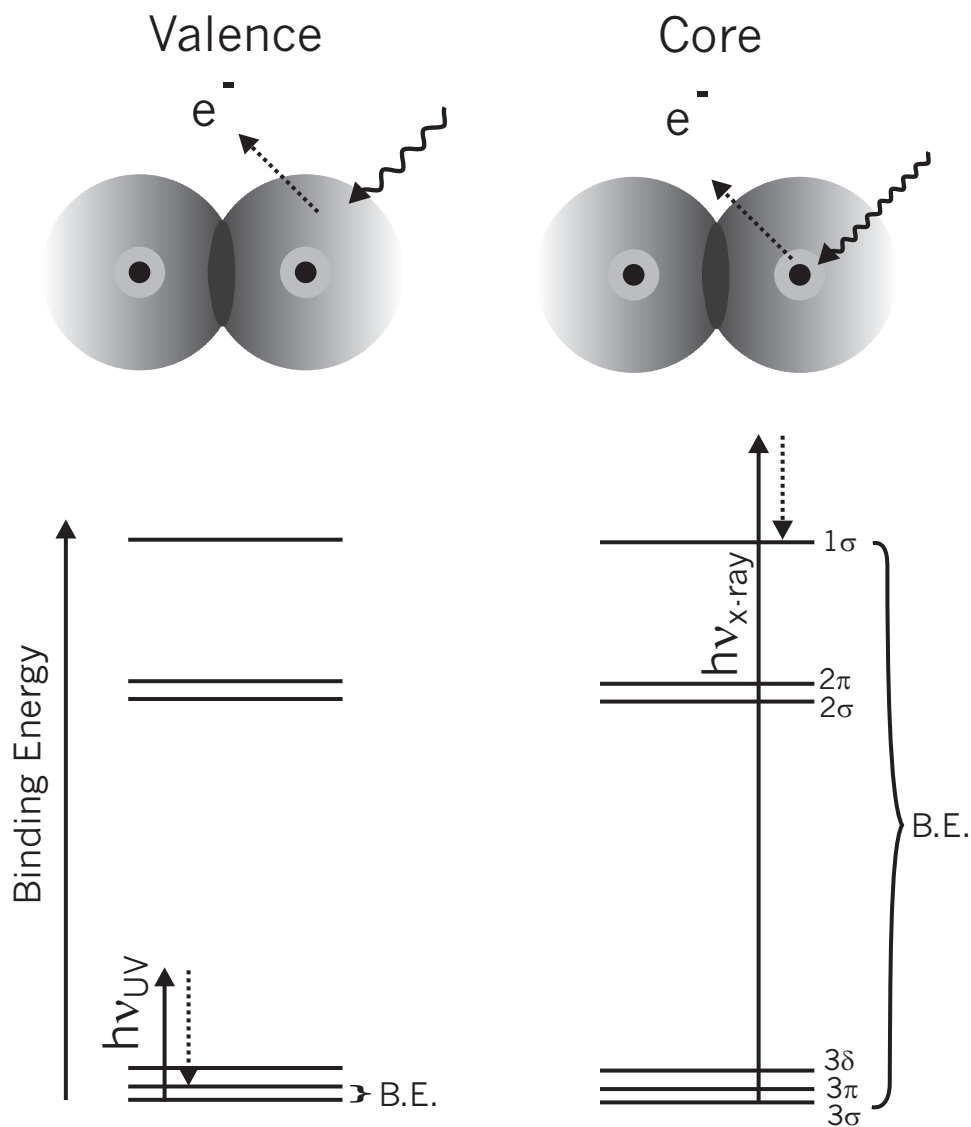


Figure 1.2: **Top:** A pictorial representation of a valence electron being ejected from a valence or bonding orbital with an ultraviolet (UV) photon, and a core electron being ejected from an inner orbital with an x-ray photon. **Bottom:** The electron energy level diagram of the above pictures. On the left, the UV photon has sufficient energy to eject the 3π electron. On the right, a x-ray photon is needed to eject the 1σ electron. The dotted arrows represent the energy of the ejected photoelectron. Binding energy (B.E.) is defined as the energy with which an electron is bound to the nucleus.

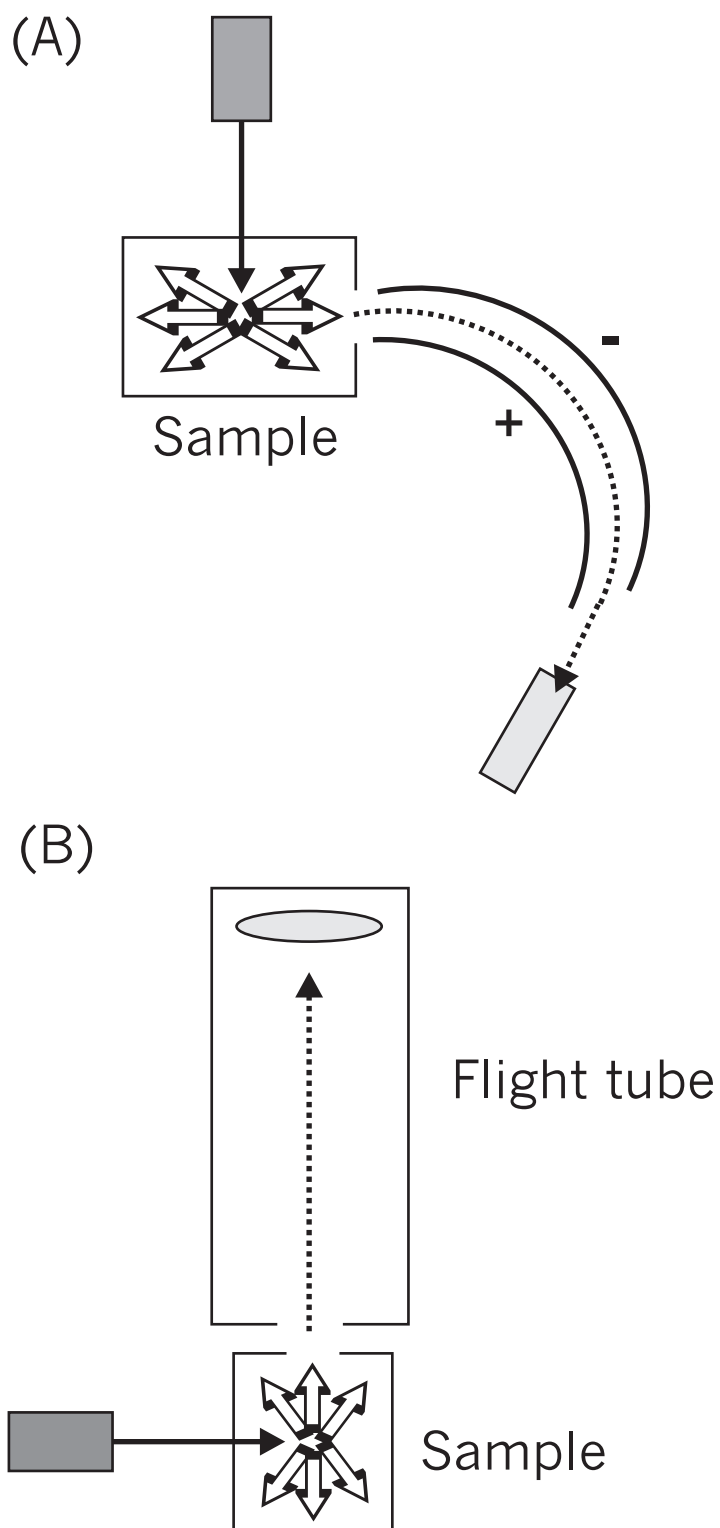


Figure 1.3: (A) A schematic of an electrostatic analyzer where electrons are energy separated by their velocities. Objects shaded with dark gray represent the photon source and the light gray objects are the detectors. The dotted line represents the electron path through the analyzer. (B) A time-of-flight photoelectron analyzer where electrons are energy separated by their arrival time to the detector.

electrons are energy separated based on the arrival time of the electrons to a fast response detector at the end of a long flight tube (Fig. 1.3(b)). The time of arrival is related to the energy of the electrons by further expanding equation 1.2:

$$E_{pe} = \frac{1}{2}m \left(\frac{d}{t} \right)^2, \quad (1.3)$$

where d is the distance traveled by the electron (usually fixed) and t is the time-of-flight. The latter is the type of energy analysis used for the data presented in this thesis.

The technique of photoelectron spectroscopy has several variations. First, the probe wavelength is scanned and total photoelectron signal is detected. Here an enhancement in the signal occurs when the incident photon energy is equal to an electronic or vibrational resonance in the atom or molecule under study, and often has similar features as in an absorption spectrum. A further extension of this first technique is to allow fast kinetic energy photoelectrons to escape and collect the low kinetic energy electrons so that only threshold resonances are measured. A second type of measurement fixes the probe wavelength and scans the energies of the photoelectrons. The energies of the photoelectrons in turn reflect the binding energies of the electrons in the atom or molecule. Coincidence methods are included in this second category, where the electron energies are scanned in coincidence with an ion of a certain mass.

For ultraviolet photoelectron spectroscopy, the He (I) lamp was once the most common light source used. It produces radiation at 584 Å, or 21.2 eV. This photon energy is enough to ionize the electrons in the valence orbitals for almost any molecule. Now, synchrotron light sources are the predominant choice as described below. An example of the ultraviolet photoelectron spectrum of a simple molecule is given in Fig. 1.4, where the photon energy is fixed and the photoelectron energies are measured. There are several noticeable features that give important information about bonding in the HBr molecule. After the molecule is ionized, the outermost orbital (the orbital with the lowest ionization energy) is split into two distinct energy peaks. These arise from the well understood phenomenon of spin-orbit splitting. The electron has a spin and that electron spin can interact with other electron orbitals or its own orbital an-

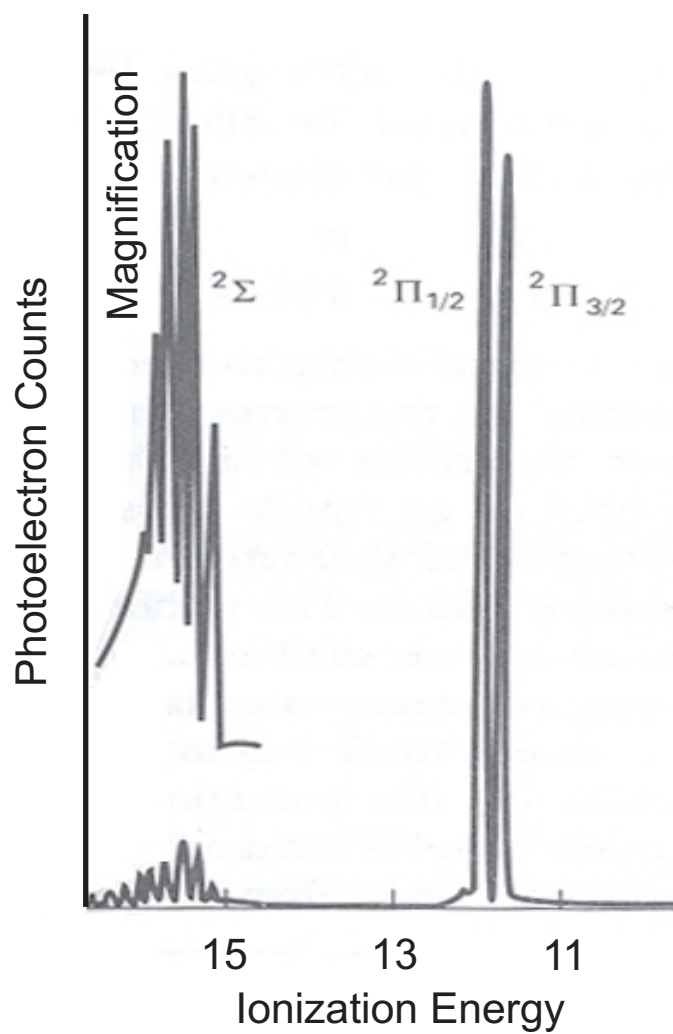


Figure 1.4: The photoelectron spectrum of HBr as a function of ionization energy. The Σ and Π labels are term symbols describing the final state of HBr^+ . Spectrum taken from ref. [1]

gular momentum. This interaction causes a splitting of the orbital energies, which results in a doublet peak in the photoelectron spectrum. The series of peaks at a higher ionization energy result from sub-energy levels in the electron orbital, or vibrational energy levels. When a bonding electron is ejected, the H-Br^+ molecule can be excited to higher vibrational energy levels, and thus the ejected electrons can lose energy, giving a series of photoelectron peaks.

The field of x-ray photoelectron spectroscopy as a technique has gained momentum in the last several decades with the introduction of synchrotron sources, a light source produced from the acceleration of electrons in a storage ring. Synchrotron sources are capable of generating light from the infrared (μm wavelengths) to the hard x-ray region (\AA wavelengths) of the electromagnetic spectrum. An example of the results from an experiment using synchrotron radiation is given in Fig. 1.5 from ref. [2]. In this experiment the 3d core electron energies of Br are measured for different Br-containing compounds. The observed photoelectron spectra (using a photon energy of 96 eV) demonstrate the principle of chemical shifts, where the energies of electronic orbitals of a particular atom shift depending on the nature of the atom on the other side of the chemical bond. For example, the Br atom in the Br-Br bond gives core level energies of ~ 78.5 and 77.5 eV (again due to spin-orbit splitting), while the Br atom in the C-Br bond in CH_3Br gives core level energies of ~ 77.3 and 76.3 eV.

1.2 Time-resolved photoelectron spectroscopy

We have seen that photoelectron spectroscopy (both valence and core level) has already given us a wealth of information about bonding in molecules. As the understanding of chemical bonding has progressed, scientists have begun to ask new questions. For instance, how do the electrons in a molecule rearrange when one electron is excited to a higher energy orbital? How do chemical bonds form in time during a chemical reaction? How does a chemical bond break in real time? The experiments presented in this thesis attempt to shed a new light on these fundamental questions.

To address the question of molecules in excited electronic states, a two-photon, two-

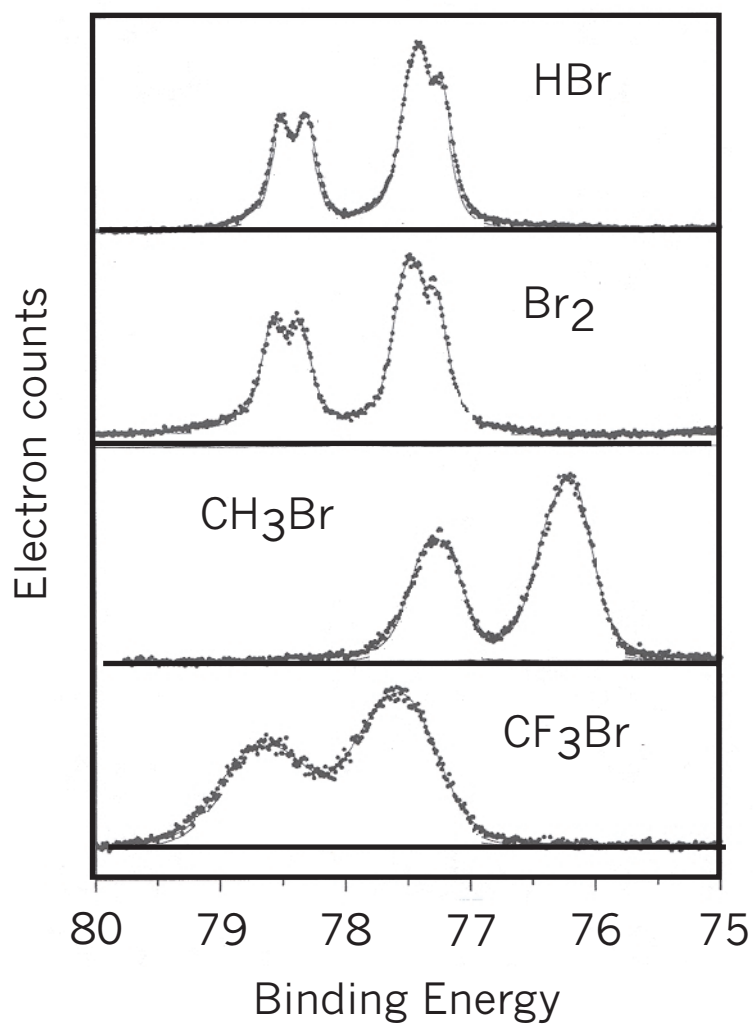


Figure 1.5: Core level photoelectron spectra of HBr, Br₂, CH₃Br and CF₃Br showing the shifting of the 3d Br core levels due to chemical bonding (taken from ref. [2]). Fine structure splitting of the ion states is also present in the spectra.

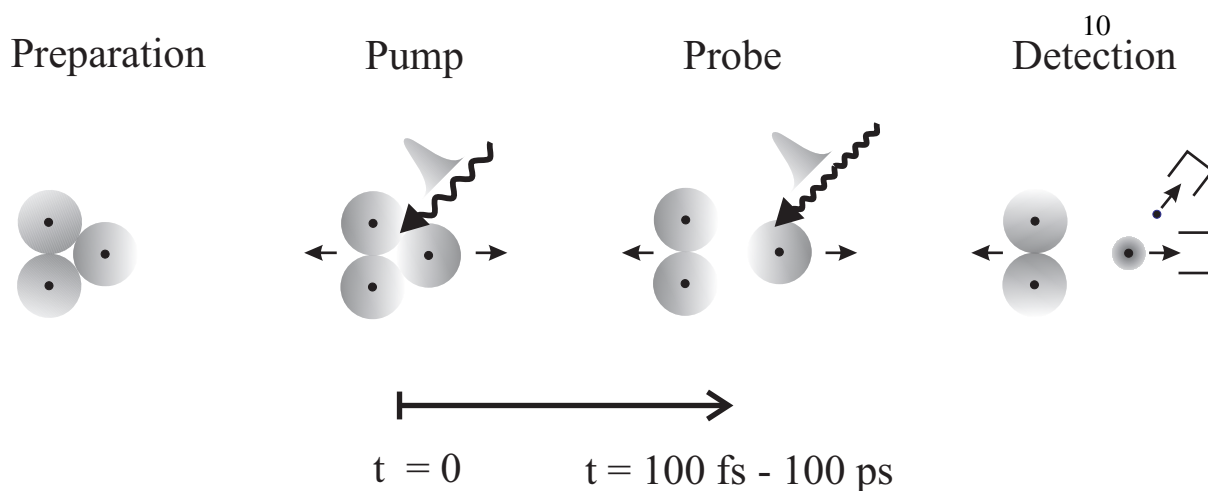


Figure 1.6: A pictorial representation of time-resolved pump-probe photoelectron spectroscopy. The sample molecule is pumped into an electronically excited state with a visible laser pulse. At varying time delays after the pump pulse, a probe laser pulse ionizes the molecule and the photoelectrons are analyzed at each time delay.

color experiment coupled with photoelectron spectroscopy can yield information on the energy redistributions of an excited molecule. A visible photon is used to promote an electron into a higher energy orbital, perturbing the entire electron distribution in the molecule, and then a UV or soft x-ray photon (via photoelectron spectroscopy) is used to measure the energies of the electrons. The related two-photon technique of Raman spectroscopy has yielded vibrational and rotational structure of a large number of molecules.

The processes of bond forming and breaking happen on extremely fast time scales, on the order of 10^{-12} to 10^{-15} seconds. With the invention of ultrafast light sources (lasers that generate very short pulses of light), photoelectron spectroscopy can be extended into the time-resolved realm. Time-resolved photoelectron spectroscopy aims to measure the electron distribution in a molecule as it is going through a transient process, such as dissociation. In general, one ultrafast pulse excites the system under study, and a second ultrafast pulse probes the system at varying time delays by ionizing the molecule and collecting the electrons produced (see Fig. 1.6). Ejected photoelectrons reflect the initial binding energies of the electrons in the molecule, therefore the time-dependent electron energy redistribution can be monitored.

Several research groups have demonstrated the important information gained by time-resolved photoelectron/photoion spectroscopy with visible and UV pulses, including characterization of bound and repulsive electronic states [7, 8, 9], photodissociation and recombination dynamics of negative ions in size selected clusters [10, 11, 12, 13, 14, 15], fast dissociation of Rydberg states [16], and non-adiabatic dynamics of a dimer molecule [17]. An example is shown in Fig. 1.7, where the solvation dynamics of $I_2^-(Ar)_{20}$ clusters were measured on an ultrafast time scale by excitation of the I_2^- chromophore with a 780 nm pulse followed by multi-photon ionization of the excited ion and analysis of the photoelectron energies[3]. The two photoelectron peaks observed are attributed to the spin-orbit states of the I atom ($^2P_{3/2}$ and $^2P_{1/2}$), a result of ionizing the I^- product. The shift in the photoelectron spectrum at early time delays is a reflection of the shifting electron energies as the I_2^- bond is broken. At later times, the photoelectron spectra shift the opposite direction, showing a recombination of the I^- and I fragments due to the surrounding cage of Ar atoms. Thus, it is demonstrated that time-resolved photoelectron spectroscopy is successful at measuring a changing electron distribution in a dynamic system.

1.3 Harmonic generation

In the experiments presented here, we extend the possibilities of time-resolved spectroscopy by combining it with a novel pulsed soft x-ray source. This source originates from a technique called high-order harmonic generation, where an ultrafast Ti:Sapphire laser is focused into a rare gas jet and odd harmonics of the laser are created (from the 3rd to 65th). The properties of the generated light are laser-like, producing coherent, directional, ultrafast light pulses with photon energies from ~ 5 -100 eV. With this range of energies, both valence and core level photoelectron spectroscopy are possible, as will be demonstrated in later chapters. Due to the ultrafast nature of the high harmonic pulses, time-resolved spectroscopy is also possible, where a pulse from the master laser is used as a pump, and the harmonic pulse is used as a probe.

Since the first harmonic spectra were obtained in 1987 [18, 19], an extensive amount of

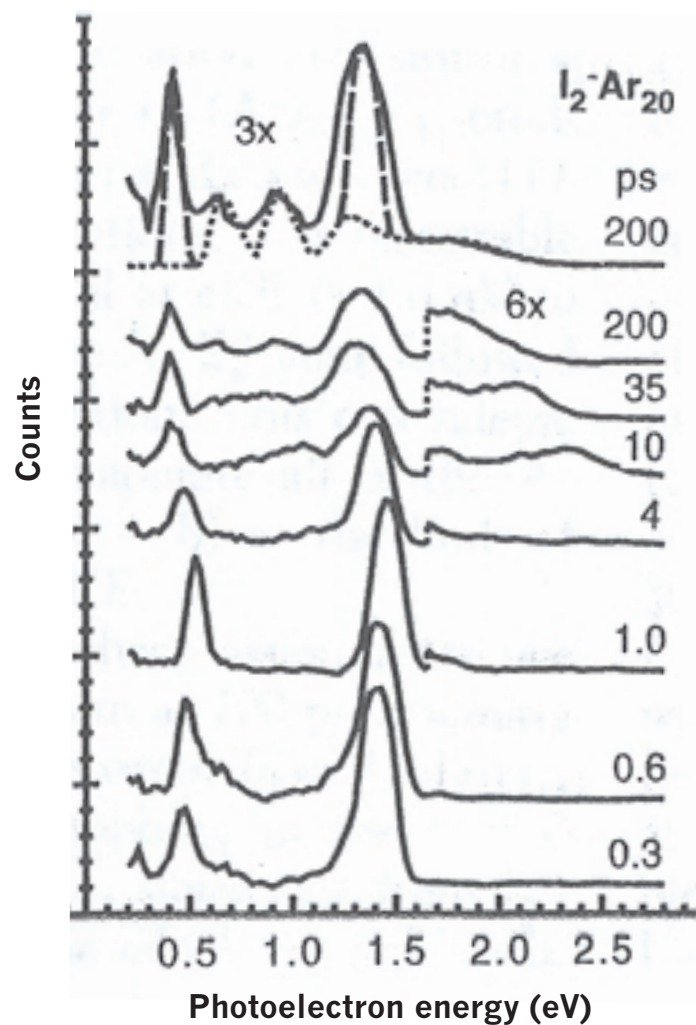


Figure 1.7: An example of a time-resolved photoelectron experiment from ref. [3]. The photoelectron spectrum of $I_2^-(Ar)_{20}$ clusters is shown at various time-delays between the pump and probe pulses.

research has been done to understand the high-order harmonic generation process as well as the properties of the resulting VUV/soft x-ray light. There are many unique characteristics of the harmonic generation process itself, which have been studied through both experiment and theory. It has been found that the extent of harmonic generation depends on several factors, such as the nature of the rare gas medium, several aspects of the focusing conditions and spatial mode of the fundamental laser in the non-linear medium [20], and the length and chirp of the fundamental pulse [21].

To a large extent, theory has successfully modeled these behaviors [22, 23], and the basic process of generating high-order harmonics is well understood. A semi-classical model can qualitatively describe the harmonic generation process, in which the electron tunnels through the barrier formed by the Coulomb potential and the intense laser field. The electron then recombines with the parent atom upon reversal of the optical field, releasing coherent high-order radiation at odd harmonics of the fundamental wavelength [24] (see Fig. 1.8). However, the semi-classical model is unable to predict detailed spectral characteristics; hence, quantum models [25, 26, 27] are required for a more complete description of harmonic generation, and are discussed in more detail in chapter 3.1.

1.4 Coupling the high harmonic source and time-resolved photoelectron spectroscopy

The use of a pulsed high-harmonic soft x-ray source to probe ultrafast chemical dynamics has several advantages. First, probing with a soft x-ray pulse allows the extension of ultrafast photoelectron spectroscopy into the realm of gas phase neutral molecules, without the need for a multi-photon probe step. Multiphoton probe steps, while effective, still have limitations in total probe energy and can cause resonance effects with the host of electronic states in even simple molecules. Though some neutral gas phase molecules have accessible ion states within the ultraviolet region, the choice of target molecules need not be limited by the energy of the probe. While soft x-ray probe wavelengths have the disadvantage of a large background due to ground

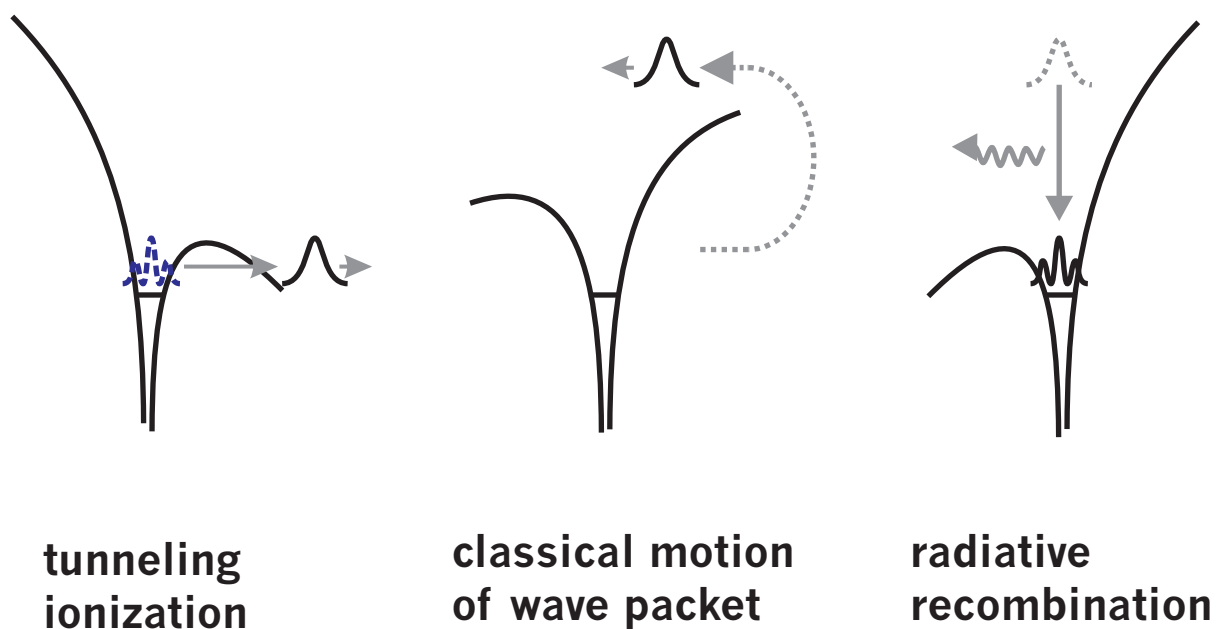


Figure 1.8: A classical picture of high-order harmonic generation with an ultrafast laser. The coulomb potential of the atom is perturbed in the presence of the strong laser field, and tunneling ionization of the electron occurs. The free electron gains energy in the electric field (U_p , ponderomotive potential). As the optical field changes phase, the coulomb potential also oscillates and causes recombination of the electron with the atom, accompanied by the release of a high energy photon.

state absorption from the neutral molecule, careful background subtraction with the use of an optical chopper to sample every other pulse with the pump on/off can overcome this limitation. The large range of photon energies obtained by high-harmonic generation creates a source that is capable of ionizing into both the ground and multiple excited states of the target molecule. This extends the realm of information that can be gained on a particular system, as cross-sections from neutral excited states to various ion electronic states may not only be different, but can also change with time as the neutral excited state wavepacket evolves. Additionally, the versatility of a high-harmonic source allows both valence and core-level time-resolved spectroscopy, giving a complete picture of the energy redistribution within the molecule. While valence level photoelectron spectroscopy yields a wealth of information, how the core level electron energies change upon excitation of a valence electron is not well understood. Core level spectroscopy also gives a site specific probe of atoms in molecules that contain two or more types of atoms, since the core level energies are specific to particular atoms. For example, in a simple molecule like IBr, the core level signature (4d) for the I atom is in the 50 eV region, while Br (3d) levels are in the 70 eV region.

Other groups have demonstrated the application of time-resolved surface photoelectron spectroscopy with soft x-ray light. Picosecond dynamics of electron-phonon interactions on thin organic films was measured by Probst and Haight [28], with a 3.5 eV excite pulse and a 22.4 eV probe pulse, the 11th harmonic of 640 nm. Ultrafast hot electron dynamics on a Pt surface were observed by Siffalovic, et al [29], by focusing a visible and 70 eV high-harmonic pulse on the surface and collecting the photoelectrons from the Pt surface. Lei, et al [30], observed a change in a chemical bond between O₂ deposited on a Pt surface on a sub-picosecond time scale using a visible pump pulse and the 27th harmonic of 800 nm as the probe pulse.

1.5 High-order harmonics and surface photoelectron spectroscopy

Photoelectron spectroscopy has also been used extensively as a probe for surface structure and bonding in condensed phase materials. As part of an internship program, I had the op-

portunity to work on another instrument designed to use a similar harmonic generation source for surface photoelectron studies. Since the internship was at IBM, improving computer components and the speed with which they are fabricated is high priority. To make a complex computer chip requires 20 layers of microscopic circuitry on a Si wafer. Each layer is patterned onto the Si wafer with a device called a photomask. Fig. 1.9 demonstrates the patterning process, where a light source is incident upon the photomask, a high purity quartz plate with images of the circuit, and the circuit pattern is transferred to the Si wafer.

These photomasks are expensive to make and the ability to precisely repair flaws in the patterns permits a significant reduction in cost and time of chip production. The photomask patterns consist of the deposition of heavy metals on the quartz surface, such as Cr or W. The use of femtosecond ultrafast lasers has already proven to be an effective tool for precise removal of unwanted metal material, such as bridges between small parts of the circuit pattern [31]. The other component in mask repair is the replacement of obliterated or chipped metal materials. Deposition and detection of Cr metal without the use of high-temperature ovens, which might further damage the photomask, is the aim of the surface photoelectron spectroscopy experiments. A gaseous metal coordination compound, $\text{Cr}(\text{CO})_6$, is thought to be a solution to metal-oven deposition. $\text{Cr}(\text{CO})_6$ is deposited on the surface and the surface is subsequently cooled with liquid N_2 . The CO ligands are then photolyzed with a UV laser beam in the areas in need of repair, leaving only the Cr metal on the surface. The remaining $\text{Cr}(\text{CO})_6$ is released upon heating. To begin to characterize the feasibility of this process, it is necessary to find a way to deposit and detect the Cr on a Si surface. Since ultrafast photoelectron spectroscopy is surface sensitive, a high-harmonic source can be used to detect the core level photoelectron signature of Cr (3p) after it is deposited on the surface. Eventually the dynamics of the deposition of Cr via $\text{Cr}(\text{CO})_6$ can also be monitored using time-resolved photoelectron spectroscopy.

In this thesis I describe in detail results obtained using the novel combination of time-resolved photoelectron spectroscopy and a visible/UV pump coupled with a soft x-ray probe. The harmonic generation source and the properties of the incident soft x-ray radiation are out-

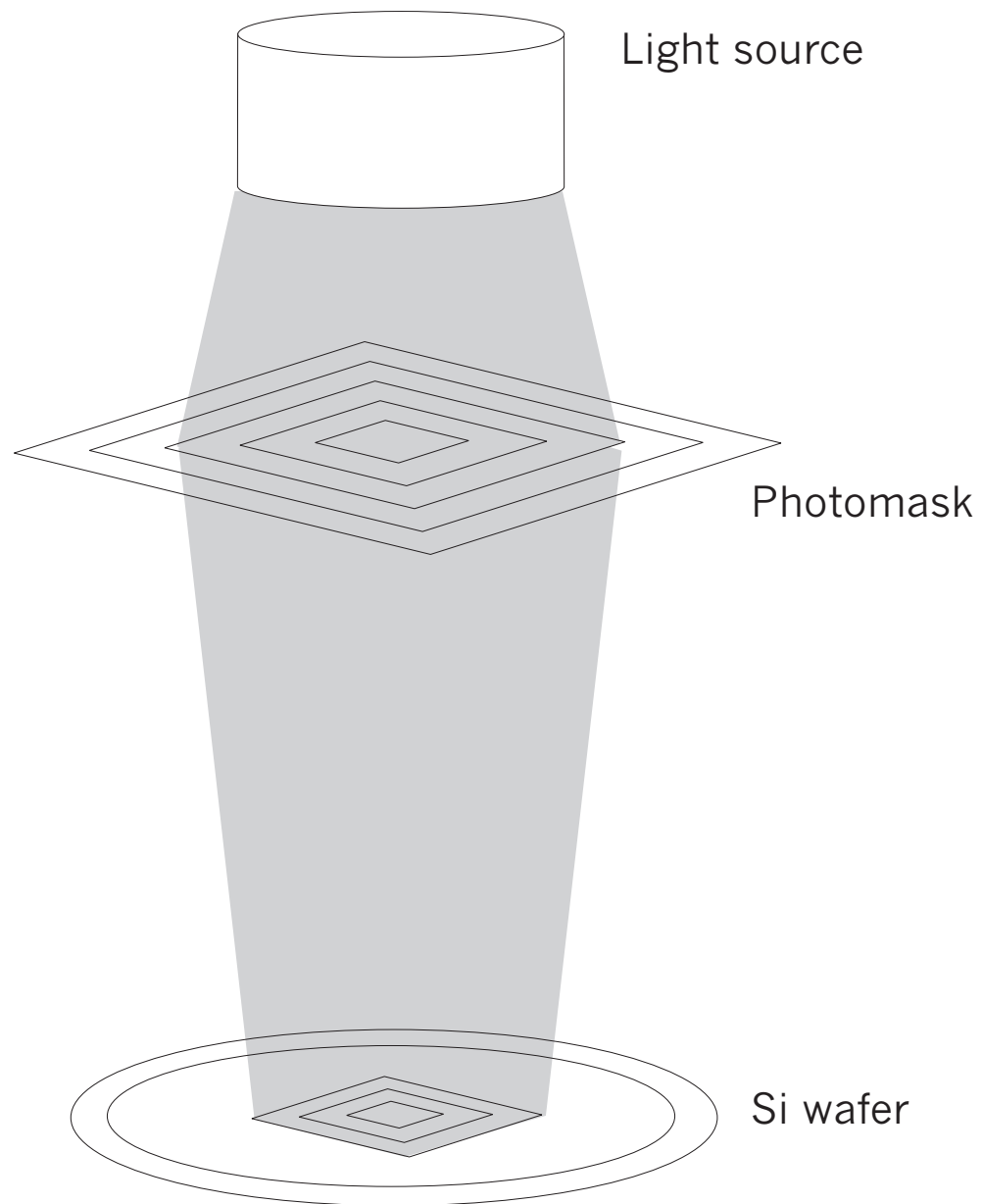


Figure 1.9: The process of imprinting circuitry on a Si wafer using a photomask. The mask is made of high-quality quartz with an image of the circuit deposited on the surface. Photons from a light source are incident on the mask and the pattern is written on the Si wafer.

lined, including a demonstration of tunability and control of the harmonic source, measurements of the energy bandwidths of generated harmonics, and several examples of soft x-ray valence and core level photoelectron spectroscopy of gas phase atoms and molecules, as well as condensed phase samples. Techniques for calibrating the overlap and temporal width of the pump and probe beams are discussed, and above threshold ionization cross-correlation traces between pump and probe beams are shown. The photoelectron spectrum of the bound B state of Br_2 is measured with a 527 nm excitation laser and a 17th harmonic probe. The dynamic photodissociation of Br_2 is observed in a 400 nm pump- 17th harmonic probe set-up, demonstrating the ability to monitor a gas phase reaction in real time.