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Mode specific photoionization dynamics in polyatomic molecules

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MODE SPECIFIC PHOTOIONIZATION DYNAMICS IN POLYATOMIC MOLECULES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Department of Chemistry

By,
Gerald Jeffery Rathbone
B.S. Wheeling Jesuit College, Wheeling WV, USA 1996
December, 2002
The Master said: “I spent all day without taking food and all night without taking any sleep. It would have been better if I spent my time in learning.”

Confucius
To Jen, thank you.
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I could not have earned this degree without the support and help of many people: Erwin Poliakoff, who seemed to have unlimited patience with me; my family: Mom, Greg, Michelle, Mike and the rest of my family everywhere; my friends Ed, Keith, the Gibbons, the Porters and all my many friends and loved ones, you know who you are; finally, Jen without her love and support over the many years, I wouldn’t have accomplished this. I owe her the biggest thanks of all.
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ABSTRACT

The work presented in this dissertation presents new work on polyatomic photoionization. In these investigations, the broad range behavior of both allowed and forbidden vibrational modes in linear triatomic systems were studied to understand mode specific aspects of photoionization. The current study is made possible by the experimental strategy of exploiting high resolution photoelectron spectroscopy and the high brightness of third generation synchrotron radiation sources. The data is taken typically tens of eV’s past the ionization potential. The strategy that I employ is to probe alternative vibrational modes which are frequently affected differently following resonant ionization. Such vibrationally resolved data can be used to understand how the correlation between vibration and electron energy reveals microscopic insights into the photoelectron scattering process. Moreover, the mode specific behavior contains a wealth of information not only regarding allowed transitions, but also contains information on how forbidden transitions gain surprising amounts of intensity. A previously overlooked mechanism for the appearance of forbidden nontotally symmetric vibrations was discovered – resonantly amplified vibronic symmetry breaking. The photoelectron the culprit for the symmetry breaking which induces the excitation of nominally forbidden vibrational excitations. In a more general sense, these results will demonstrate that some fundamental spectroscopic approximations are not always valid, and can lead to surprising consequences.
CHAPTER ONE : INTRODUCTION

The motivation of any dissertation dealing with spectroscopy attempts to answer some version of the question: “How does light interact with matter?” The particular type of spectroscopy I will describe involves short wavelength radiation with sufficient energy to ionize the targets being investigated. The specific targets of the light in my studies are simple molecules in the gas phase, most of them being polyatomic systems. Specifically, I observed the way nuclear and electronic degrees of freedom couple during photoionization. This issue has never been investigated for all the vibrational modes in polyatomic molecular systems in a systematic way previously, and the results described later demonstrate that qualitative new insights emerge from such investigations. There are a number of approximations that are fundamental to photoionization. This work will test the validity of these approximations and reveal when they are valid. Studies such as these develop a richer understanding of photoionization scattering dynamics, and the understanding of photoionization dynamics for simple systems has led to interesting results for other spectroscopic applications. As an example, note that the results presented here using ultraviolet ionizing radiation have interesting parallels and applications for experiments such as using x-ray ionizing radiation, such as X-ray Absorption Near Edge Structure, XANES. ¹

To begin let us first consider photoionization. In the classical “cartoon” of photoionization, a photon of short wavelength interacts with a free atom or molecule. The photon can be annihilated, and the energy of the photon can be imparted to the molecule. This will cause this molecule to ionize. It is usually thought that the electron is simply “plucked” out of the molecular framework, i.e., it does not encounter any
barriers to ionization. However, it has been well documented for diatomic systems that there can be strong coupling between nuclear and electronic degrees of freedom. \(^2\) The products of photoionization, i.e. the photoion and the photoelectron, can be studied to understand photoionization scattering dynamics, i.e., the microscopic aspects of the photoelectron escape from the molecular framework and their consequences on the resulting spectra. We explore the broad range behavior of photoionization and test the validity of these simple assumptions. The work I present shows that the outgoing photoelectron imparts oscillator strength to nominally forbidden transitions.

The work exploits several experimental tools to study the photoionization dynamics over a broad range. The first is the radiation source itself, which is tunable synchrotron radiation for all of these studies. Second is high-resolution photoelectron spectroscopy, this is the traditional approach to the studying the broad range aspects of photoionization. Historically, vibrationally resolved photoelectron spectroscopy experiments performed synchrotron radiation as the ionization source were limited to simple systems such as diatomics and systems with large vibrational frequencies. The high brightness from most state-of-the-art synchrotron sources (such as the Advanced Light Source facility at Lawrence Berkeley Laboratory) allows one to probe even low frequency molecular vibrations over a broad range of excitation energies. This is the first time these two experimental tools have been combined to study the broad range characteristics of polyatomic molecular photoionization.

Tunable synchrotron radiation from less “bright” (i.e., second generation) sources is also exploited in this study. These sources are not as bright as third generation sources, but are still extremely useful for well-selected studies, as will be shown. The
experimental strategy employed with such a source is to use dispersed fluorescence from electronically excited molecular photoions. Detection of the final state ionic fluorescence provides similar information to photoelectron spectroscopy. The resolution of ionic fluorescence is not coupled to the excitation bandwidth, so experiments can be performed which provide detailed information on energy deposition in the photoion even if the excitation source does not have a particularly narrow bandwidth, as opposed to the photoelectron measurements that comprise the bulk of this dissertation.

This dissertation presents the first broad range studies of polyatomic systems where all of the vibrational degrees of freedom have been investigated following photoionization. Specifically, the main focus is on linear triatomic systems. The broad range of energies studied (ca. 100 eV) allows us to understand how systems respond as the photoelectron wavefunction evolves with energy. Similarly, the ability to study all of the vibrational degrees of freedom permits us to understand how the photoelectron responds to selected changes in molecular geometry. A new depth of understanding becomes possible given such a systematic approach. It should be emphasized that there have been some previous studies \(^3\text{-}^6\), but they have been limited in one way or another by experimental constraints that do not impede the investigations described in this dissertation. New insights emerge in a natural way from this more complete approach of studying all of the vibrational degrees of freedom.

Chapter 2 details general spectroscopic considerations, and also provides some background relevant to the topic of molecular photoionization. The Franck-Condon approximation is central to discussions of vibrational structure in electronic transitions.
Other theoretical background, such as vibronic coupling and intrachannel vibronic interactions will also be developed in detail here.

Chapter 3 reviews the experimental aspects and strategy for studying photoionization. I will explain the use of synchrotron radiation further, including the significance of using radiation from undulators in order to perform high resolution molecular photoelectron spectroscopy, as well as the technique of dispersed fluorescence spectroscopy as a means to produce highly resolved vibrational data from photoions. Additionally, the advantages and disadvantages of both photoelectron spectroscopy and dispersed fluorescence spectroscopy will be discussed in this chapter.

Finally, in the later chapters I will present the results and discussion for the studies that have been performed. Chapter 4 describes the dispersed fluorescence investigation on $4\sigma^{-1}$ photoionization of CO. This study completes a series of studies into how the $2\sigma_u^{-1}$ photoionization of N$_2$ compares with the valence isoelectronic $4\sigma^{-1}$ channel of CO. In fact, they are quite different, and the significance of the differences will be described. The subsequent chapters describe the investigations into vibrationally resolved photoelectron spectroscopy of a few linear triatomic systems. All of these investigations include information on all of the vibrational degrees of freedom. All include very wide spectral coverage and are able to discern patterns and systematic behavior in a way that has never been possible previously. More specifically, all of these triatomic systems exhibit a surprising propensity to exhibit symmetry forbidden vibrational excitations, namely, the excitation of single quantum excitations of nontotally symmetric vibrations. Such transitions are forbidden in the traditional formulation of molecular spectroscopy, and we find that the mechanism responsible for such behavior is
not well-established in the literature. My work shows that such traditional pictures of molecular spectroscopy must be generalized to account for the behavior that is observed, as it is likely to be widespread. The specific systems investigated include $4\sigma_g^{-1}$ photoionization of CO$_2$ (Chapter 5), $5\sigma_u^{-1}$ photoionization of CS$_2$ (Chapter 6), and the $7\sigma^{-1}$ photoionization of N$_2$O (Chapter 7).
CHAPTER TWO : SPECTROSCOPIC BACKGROUND

Quantum theory was developed to describe the behavior, including the macroscopic properties, of microscopic particles. Molecular spectroscopy is one of the main tools in the intellectual machinery used to study quantum systems. Fundamental to the study of molecular spectroscopy is the Born-Oppenheimer approximation (BOA). The BOA states that electrons see the nuclei as nonmoving charges. In essence, the electrons’ motions are so fast that they constantly adjust to the relatively slow motion of the nuclei that results from vibrational and rotational motion. As a result, it is possible to separate the nuclear and electronic motions. More specifically, this approximation allows the total wave function to be separated into the product of electronic and vibrational wave functions. (For the work described in this dissertation, rotational resolution is not possible and the discussion neglects rotational motions for simplicity.) For simple systems the Schrödinger equation can be straightforwardly solved. A specific spectroscopic method that will be described in detail below is photoelectron spectroscopy. Photoelectron spectroscopy is commonly used in modern chemistry laboratories because it provides simple and detailed information on atomic, molecular, ionic, and chemically reactive systems (e.g., clusters and radicals). Photoelectron spectroscopy is performed by illuminating a target system with monochromatic radiation that exceeds the ionization threshold of the system while monitoring the photoelectron intensity as a function of the electron kinetic energy. Electrons that are weakly bound (e.g., outer valence electrons) are ejected with higher kinetic energies while electrons that are strongly bound are ejected with lower kinetic energies. Thus, such measurements provide a detailed map into the (N-1) electron system created by the absorption of the...
ionizing radiation. Photoelectron spectroscopy has been used to document breakdowns in the Born-Oppenheimer approximation \(^2,15-19\), and one such example is vibronic coupling. However, I will show that the evidence that is used to ascribe various observations as violations of the Born-Oppenheimer approximation can also be shown to result from other mechanisms, and this will be described in the discussion sections of the later chapters. Because the Born-Oppenheimer approximation is necessary for describing the background literature, it will be covered briefly in this chapter.

My studies will demonstrate that a more significant mechanism for the observation of forbidden transitions is the violation of the Franck-Condon approximation. In particular, it is possible for the observation of symmetry forbidden transitions to result from violations of the Franck-Condon approximation rather than the BOA. As a result, this chapter will focus in some detail on the derivation of the Franck-Condon approximation. The Franck-Condon approximation is central to the study of molecular spectroscopy. It is described in terms of the BOA framework, so it is possible to have deviations from the Franck-Condon approximation while still obeying the BOA. The Franck-Condon approximation freezes nuclear motion for electronic transitions, therefore the electron moves vertically between potential energy surfaces during electronic transitions.

### 2.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is central in our vocabulary describing most aspects pertaining to molecular dynamics, especially in the description of spectroscopy; it simply decouples the nuclear and electronic degrees of freedom, and gives us the language of potential energy surfaces. Without this separation of nuclear and
electronic degrees of freedom, complex Hamiltonians would be needed even for the simplest molecular systems. Thus, the Hamiltonian for a molecular problem is greatly simplified when the BOA is applicable, and solutions to the Schrödinger wave equation can be generated with relative ease. The BOA approximation has been known to break down; some well-studied examples are vibronic coupling effects in photoelectron spectroscopy.\(^2,^{15-19}\) Occasionally, the excitation of single quanta of nontotally symmetric vibrations occurs in electronic transitions. One such example is the observation of the forbidden electronic transition \(A^1B_{2u} \rightarrow X^1A_{1g}\) transition of benzene.\(^20\) The \(A \rightarrow X\) transition is forbidden by symmetry, but has been observed with moderate intensity in the near UV region. The \(0 \rightarrow 0\) transitions are not observed, but \(\Delta v_6 = 1\) transitions are prominent. The \(v_1\) ring breathing mode is also observed. The \(v_1\) mode is totally symmetric and is an allowed transition. The \(v_1\) mode occurs in combination with an odd number of non-totally symmetric vibrations, typically the \(v_6\) mode. The \(A \rightarrow X\) becomes allowed by vibronic coupling and this was first explained by Herzberg and Teller.\(^2\) The Herzberg-Teller theory of vibronic coupling is a breakdown of the Born-Oppenheimer approximation, since nuclear and electronic degrees of freedom can no longer be separated. For these cases, one must consider the total vibronic symmetry, \(\Gamma^{el} \otimes \Gamma^{vib} = \Gamma^{vibronic}\). For the benzene example, the vibronic symmetry of the ground state in the ground vibrational level is \(A_{1g}\), while the vibronic symmetry of the excited state is \(B_{2u} \otimes e_{2g} = E_{1u}\). If the vibrational and electronic wavefunctions are considered inseparable, then the transition moment integral is now nonzero. Inclusion of a single quantum of a nontotally symmetric vibrational mode changes the overall symmetry of the state and permits the transition. It will be a goal of this thesis project to determine
whether the BOA breakdown is appropriate for all of the instances of forbidden vibrational excitations in photoionization that have been cited in the past. Vibronic coupling is almost always cited as the reason for the appearance of nontotally symmetric (forbidden) transitions in polyatomic spectra. For example, Baltzer et al.\textsuperscript{21} rationalized the appearance of the forbidden bending excitation ($\nu_2$) in the spectrum of the CS$_2^+$ ($B^3\Sigma_u^+$) state with the statement, “The excitation of odd quanta of the $\nu_2$ mode can be explained by vibronic interaction with the $X^2\Pi_g$ state, which implies that the interaction spans an energy interval of 4.5 eV.” This quote gives a sense of how well accepted the Herzberg-Teller coupling mechanism is whenever forbidden vibrational excitations are observed. New results presented here demonstrate that the Herzberg-Teller mechanism is not the only plausible explanation for the appearance of symmetry forbidden vibrational excitations.

Now I begin with the quantitative aspects of the spectroscopic background, and this begins with some background into the Born-Oppenheimer approximation. Only a brief discussion of the Born-Oppenheimer approximation will be presented here, as only a few points are germane for the data analysis that follows in later chapters. A more detailed explanation can be found in molecular spectroscopy texts.\textsuperscript{2,22} In equation (2.1) the complexity of the general molecular problem is shown by considering the total Hamiltonian for a diatomic molecule with n electrons:

\begin{equation}
\hat{H} = \sum_{n=1}^{2} \frac{-\hbar^2}{2m_n} \nabla_n^2 + \sum_{i=1}^{n} \frac{-\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{n} \sum_{N=1}^{N} \frac{Z_N e^2}{|\mathbf{r}_i - \mathbf{R}_N|} \\
+ \frac{1}{4\pi\varepsilon_0} \frac{Z_e Z_N e^2}{|\mathbf{R}_N - \mathbf{R}_e|} + \hat{H}_{so} \tag{2.1}
\end{equation}
The contributions to $\hat{H}$ include nuclear kinetic energy, the electron kinetic energy, the electron-electron repulsion, the nuclear separation and the spin-orbit coupling. To solve the current Hamiltonian is a daunting task indeed. The BOA simplifies the total Hamiltonian by freezing the internuclear separation and defining a new Hamiltonian for the electrons only, i.e., the electronic Hamiltonian $\hat{H}_{el}$,

$$\hat{H}_{el} = \hat{H} - \sum_{N=1}^{2} -\frac{(\hbar/2\pi)^2}{2m_N} \nabla_N^2 - H_{so}$$

(2.2).

The electronic Hamiltonian in Eq. (2.2) is different from $\hat{H}$ in Eq. (2.1), as it lacks the nuclear kinetic energy and spin orbit interactions.

The Coulombic forces acting on the nuclei and electrons are similar in magnitude. But when taking into consideration the relative masses of the electrons and nuclei, the motion of the electrons is going to be much faster then the motion of the nuclei. The electronic structure is solved by assuming nuclei are "clamped" or fixed in space and solving the pure electronic equation

$$\hat{H}_{el}(r, R)\psi_{el}(r, R) = E_{el}(R)\psi_{el}(r; R)$$

(2.3).

The resulting electronic states $\psi_{el}(r; R)$ will depend parametrically on $R$. The eigenvalues $E_{el}(R)$ are the potential energy curves, the electronic energies as a function of the internuclear separation $R$. The formalism was for a diatomic system. It can be generalized to polyatomic systems. The internuclear separation $R$ must be replaced with normal coordinates $Q$. The eigenvalues $E_{el}(Q)$ are now the potential energy surfaces.
The BOA fails when kinetic energy terms for the nuclear motion terms become comparable to the electronic terms. Usually these terms are small and can be neglected. These breakdowns are of interest in molecular spectroscopy and energy transfer, such as vibronic coupling in electronic spectroscopy of polyatomic molecules.

2.2 Franck-Condon Approximation Applied to Photoionization

My experiments strongly suggest that many nominally forbidden photoionization transitions arise not from a breakdown of the Born-Oppenheimer approximation, but rather from deviations from the Franck-Condon approximation. In order to understand such phenomena, it is necessary to review the Franck-Condon approximation. The classical picture of the Franck-Condon (FC) approximation states that nuclei do not have time to move while an electron undergoes a transition between electronic manifolds. It is based on the physical fact that electronic transitions are very rapid. This implies that nuclei are “frozen” and the electron undergoes a vertical transition.

To fully describe the Franck-Condon approximation, the quantum mechanical description must be explored. This will be discussed in terms of transitions between bound states, as the notation is simpler, but the central ideas can be applied to photoionization (which involves excitation to a continuum state) as well. The Franck-Condon approximation will first be described for a diatomic system. It is straightforward to generalize this to polyatomic systems, and this will be done after the simpler diatomic example is covered. First, consider a system with initial states: $|i\rangle$ going to a final state $|f\rangle$ with $\hat{d}$ being the dipole moment operator. This expression is valid for any transition, assuming that the dipole approximation is valid, which is probably true for the systems being studied.
\[ D(i \to f) = \langle f \middle| \hat{a} \middle| i \rangle \] (2.4).

The dipole approximation assumes that all parts of the system experience the same electric field at an instant in time, and such an approximation is expected to be valid providing that the spatial extent of the absorbing chromophore is small compared to the wavelength of the incident radiation. That is certainly true for these experiments, as the chromophore dimensions are on the order of 1 Å, while the wavelength of the light is on the order of hundreds of Å.

The quantity described by Eq. 2.4 is central to the discussion because the transition rate is given by the square of the amplitude of this quantity (ignoring constant factors). The eigenfunctions are products of a vibrational wave function \( \chi(R) \) and electronic wave functions \( \psi(r, \theta, \phi; R) \), where \((r, \theta, \phi)\) represent the electron’s position in spherical coordinates and \(R\) is the internuclear separation. We will neglect rotational motion, and Eq. 2.3 can be written as

\[ \hat{\chi} \psi \chi \rightarrow = \langle \psi_f, \chi_f | \hat{d} | \psi_i, \chi_i \rangle \] (2.5),

Next, the dipole moment operator can be separated into nuclear, \( \hat{d}_{nuc} \), and electronic, \( \hat{d}_{ele} \), components. The total operator is \( \hat{d}_{tot} = \hat{d}_{nuc} + \hat{d}_{ele} \). The matrix element can be written as

\[ D(i \to f) = \langle \psi_f, \chi_f | \hat{d}_{nuc} | \psi_i, \chi_i \rangle + \langle \psi_f, \chi_f | \hat{d}_{ele} | \psi_i, \chi_i \rangle \] (2.6).

The first term goes to zero because the electronic eigenfunctions belong to different electronic states and are orthogonal. To see this, express this matrix element as

\[ \langle \psi_f, \chi_f | \hat{d}_{nuc} | \psi_i, \chi_i \rangle = \langle \chi_f | \hat{d}_{nuc} | \psi_f \rangle \langle \psi_i | \chi_i \rangle \] (2.7).
While the $\langle \psi_f | \psi_i \rangle$ term cannot be separated from the nuclear integral (because the electronic wavefunctions depend parametrically on nuclear coordinates), it is identically zero at each internuclear separation owing to the orthogonality of the electronic wavefunctions.

The electronic part of the dipole moment matrix element is written as

$$ D(i \rightarrow f) = \langle \psi_f | \chi_f | \hat{d}_{\text{ele}} | \psi_i, \chi_i \rangle $$

$$ D(i \rightarrow f) = \langle \chi_f | \left[ \langle \psi_f | \hat{d}_{\text{ele}} | \psi_f \rangle \right] \chi_i \rangle $$

$$ D(i \rightarrow f) = \langle \chi_f | D_{\text{ele}}(R) \chi_i \rangle $$

$D_{\text{ele}}(R)$ is the electronic transition dipole moment. The electronic transition dipole moment depends on the incident photon energy through the final state continuum wave function. If one assumes that $D_{\text{ele}}(R)$ is a slowly varying function of $R$, then the electronic transition dipole moment can be treated as a constant and factored out. This is the key approximation of the Franck-Condon framework. The variation of the electronic dipole matrix with $R$ is neglected and an effective value, $D_{\text{ele}}(R_0)$, is used in its place, where $R_0$ is the $R$-centroid of the transition. The transition dipole matrix element is approximated by

$$ D(i \rightarrow f) = \langle \chi_f | \chi_i \rangle \left[ D_{\text{ele}}(R_0) \right] $$

The square of the transition dipole matrix is proportional to the intensity of the transition

$$ \sigma(i \rightarrow f) \propto \left| \left[ \chi_f | \chi_i \right] \right|^2 \left[ D_{\text{ele}}(R_0) \right]^2 $$

The value of $[D_{\text{ele}}(R_0)]^2$ determines the strength of the transition. $[D_{\text{ele}}(R_0)]^2$ is independent of internuclear configuration. The Franck-Condon factor is defined
as $|\langle \chi_i | \chi_f \rangle |^2$. These are the determined by the nature of vibrational wave functions and are the squares of the overlap integrals between initial and final vibrational levels. The Franck-Condon factors determine the relative intensity among vibrational bands for a given electronic transition, including photoionization transitions.

Now consider a ratio of two transition probabilities both starting from the same vibrational level and going to different vibrational final states $\nu_{1f}$ and $\nu_{2f}$. A vibrational branching ratio is defined as, $\frac{\sigma_{\nu_i \rightarrow \nu_{1f}}}{\sigma_{\nu_i \rightarrow \nu_{2f}}}$, i.e., the relative cross-sections for producing two alternative vibrational levels of an ion

$$\frac{\sigma_{\nu_i \rightarrow \nu_{1f}}}{\sigma_{\nu_i \rightarrow \nu_{2f}}} = \frac{|\langle \chi_i | \chi_{1f} \rangle |^2}{|\langle \chi_i | \chi_{2f} \rangle |^2} = \frac{q_{\nu_i \rightarrow \nu_{1f}}}{q_{\nu_i \rightarrow \nu_{2f}}} \quad (2.11).$$

This is the key result that requires some elaboration. The branching ratios are determined by the ratio of the Franck-Condon factors. There is no dependence on electronic matrix elements because these are the same for both vibrational levels and the ratio forces them to cancel one another. As a result, the ratio is independent of incident photon energy, so will be a constant as a function of photon energy. The branching ratio for an excited vibration to the ground vibrational level will have typical values of on the order of 5 to 10 % for allowed transitions for cases where the potential surfaces are similar.

However, there are several reasons that the Franck-Condon approximation fails and the branching ratios are not constant with photon energy. For example, when a potential barrier enhances the photoionization cross-section and produces a phenomenon known as a shape resonance, the dipole matrix element can depend strongly on the internuclear separation. This effect and other related phenomena have been well
documented for molecular photoionization processes. The phenomena that induce such non-Franck-Condon behavior include shape resonances\textsuperscript{11,23-26, 2,15-19}, autoionization\textsuperscript{27-30} and Cooper Minima\textsuperscript{31,32}.

While this development has been cast in terms of a diatomic example, the same framework is transferable to a polyatomic system, only the internuclear separation must be replaced by a generalized normal coordinate.\textsuperscript{2} The key aspects are identical. However, there is one difference that is discussed in detail in the following section, namely, which types of vibrational excitations are allowed for polyatomic systems.

### 2.3 Polyatomic Vibrational Selection Rules for Photoionization

It is useful to generalize the diatomic treatment in the previous section to polyatomics, because triatomic systems were the principal systems studied in this thesis project. Molecules with very high symmetry have well-defined selection rules for vibrational structure. For the Franck-Condon factor $|\langle \chi_i | \chi_f \rangle |^2$ in (2.11) to be non-zero, the direct product corresponding to the wave functions must contain the totally symmetric representation. To put this in the context of group theory the direct product of $\chi_i$ and $\chi_f$ must contain the totally symmetric representation in the point group of the molecule or ion. The vibrational ground state is always totally symmetric; therefore only totally symmetric modes are allowed to undergo single quantum excitations. This is because the direct product of a totally symmetric function and a non-totally symmetric function always transforms as the irreducible representation of the non-totally symmetric function, i.e.,

$$\Gamma_{A1} \otimes \Gamma_x = \Gamma_x,$$

where $x$ is any irreducible rep other than $A_1$. 

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Thus, one quantum of excitation for motions such as bending and asymmetric stretching are strictly forbidden within the framework of the Franck-Condon approximation. However, such features are observed, and a primary goal of this dissertation is to understand the origin of such transitions.

The vibrational wave functions for totally symmetric modes are allowed regardless of the number of quanta excited. In excitation of even numbers of quanta of asymmetric modes, the wave function contains the totally symmetric representation. So, the excitation of two quanta of bending excitation is allowed. Mathematically, this is equivalent to $\Gamma_x \otimes \Gamma_x \subset \Gamma_{A1}$, i.e., any function multiplying itself contains a totally symmetric component.

For most of the systems studied in this thesis work, the intensity of the $\Delta \nu = \pm 2, \pm 4...$ excitations are less than that of the 0-0 main line, owing to the similarity of the neutral and ionic potential energy surfaces. For the upper state (i.e., the ionic state), vibrational wave functions have maximum intensity at the symmetric position directly above the vibrational ground state.

2.4 Herzberg-Teller Effect: Vibronic Coupling

One well-established mechanism by which nominally forbidden transitions occur is vibronic coupling. This is a breakdown in the Born-Oppenheimer approximation, and one consequence is that single quantum excitations of non-totally symmetric vibrations in electronic transitions obtain oscillator strength. We will find that this mechanism is not responsible for most of the significant observations that I will describe in subsequent chapters, but it is essential to go through the analysis in order to develop a means of interpreting the data, which will be described later.
There are alternative explanations for the mechanism responsible for the appearance of nominally forbidden transitions, as discussed by Herzberg. The appearance of electronic transitions which are forbidden in a frozen geometry framework is usually referred to as “type b” vibronic interaction. An example is the benzene case discussed previously. If the transition can occur in the equilibrium geometry, but is forbidden for specific vibrational excitations, then it is referred to as a “type-a” vibronic interaction. To place this in the framework of photoionization, a “type (a)” vibronic interaction is a type of non-Franck-Condon effect with molecular vibrations that lower the symmetry of the molecule. In the Herzberg monograph, no examples are given for type-a interactions, and the aspects relevant to photoionization processes are covered.

The mechanism that I describe here is normally referred to as Herzberg-Teller coupling. If we start with the zeroth order electronic Schrödinger wave equation and Hamiltonian

\[ \hat{H}_e \psi_e^0 = E_e \psi_e^0 \]  

(2.12).

However, the complete Hamiltonian depends on the vibrational coordinates and the total Hamiltonian needs to be corrected for this perturbation. The unperturbed Hamiltonian is expanded with the power series

\[ \hat{\mathcal{H}} = \hat{H}_e^0 + \sum_i \left( \frac{\partial H_e}{\partial Q_i} \right)_{Q_i=0} Q_i + .... \]  

(2.13).

The Hamiltonian is truncated at the first term of the expansion, yielding

\[ \hat{\mathcal{H}}' = \sum_i \left( \frac{\partial H_e}{\partial Q_i} \right)_{Q_i=0} Q_i \]  

(2.14).
The excited state wave $\psi_f^0$ can now interact with the zeroth-order electronic states wave functions through the perturbation $H'$. The wave equation is expanded as a perturbation series in the usual way, i.e.,

$$\psi_e = \psi_f^0 + \sum_{k \neq f} c_k \psi_f^k \quad (2.15)$$

$$c_k = \frac{\langle \psi_f^0 | H' | \psi_f^k \rangle}{E_f^0 - E_k^0} \quad (2.16).$$

The degree of mixing of states is determined by the vibronic coupling matrix element $\langle \psi_f^0 | H' | \psi_f^0 \rangle$ (the numerator) and the energy separation of the mixing states, $E_f^0 - E_k^0$ (the denominator). The closer in energy the interacting states are to one another, the stronger the coupling. This is known as intensity “borrowing” or “stealing”. Nominally forbidden transitions can become allowed via this mechanism.

Herzberg-Teller coupling is an example of BOA breakdown. Because vibrational and nuclear degrees of freedom can no longer be separated, the total vibronic symmetry is the direct product of the vibrational and electronic states

$$\Gamma_{\text{electronic}} \otimes \Gamma_{\text{nuclear}} = \Gamma_{\text{vibronic}} \quad (2.17).$$

The selection rules apply to the total symmetry of a level. The vibronic symmetry of a level is the product of electronic and vibrational symmetries. The result is that a vibrational excitation that is considered forbidden can be observed and the intensity is dependent on the strength of the coupling to another electronic state. A simple picture of vibronic coupling is shown in figure 2.1. The electronic characteristics of the new vibrational features are most probably similar to the electronic state to which it is
coupling. As we will see in an example from the literature, this will have consequences that can be observed in the photoelectron asymmetry parameters, $\beta$.

An excellent example of Herzberg-Teller coupling influencing a forbidden transition was done by Roy et al.\textsuperscript{18} on the CO$_2^+$ ($C^2\Sigma_g^+$) state. In that study, the

![Figure 2.1 A pictorial view of vibronic coupling and how forbidden transitions gain intensity by coupling to electronic states of the same symmetry.](image)
The $v^+ = (101)$ vibration is clearly resolved in the photoelectron spectrum. This transition is forbidden, as it involves the excitation of a single quantum of the asymmetric stretching vibration, which transforms as the $\Sigma_u$ irreducible representation. The vibrationally resolved photoelectron spectrum was obtained at several energies in the range from $20 \leq h\nu \leq 28.5$ eV and they also measured the photoelectron asymmetry parameters for the ground vibrational state, (000), as well as the forbidden vibration (101). The asymmetry parameter energy dependences for the two vibrational levels did not track one another over the energy range studied. The values of the asymmetry parameters depend mainly on the electronic character of the orbital. The asymmetry parameters for different vibrational levels belonging to the same electronic state should be equal. The fact that the ground vibrational state (000) and the forbidden vibration (101) data sets did not track one another was a strong indication that the $v^+ = (101)$ forbidden level was “stealing” intensity from a different electronic state of the same symmetry. They compared the asymmetry parameter curve of $v^+ = (101)$ forbidden level to the photoelectron asymmetry parameter for the $B^2\Sigma_u^+$ state. These two curves – the $C^2\Sigma_g^+, v^+ = (101)$ and the $B^2\Sigma_u^+$ asymmetry parameter energy dependences – did track each other quite faithfully.

The analysis employed by Roy et al. was based on the observation that the $C^2\Sigma_g^+, v^+ = (101)$ was borrowing its intensity from the $B^2\Sigma_u^+$ state, i.e., they evoked a Herzberg-Teller analysis to explain the appearance of this forbidden transition. The electronic symmetry of the $(C^2\Sigma_g^+)$ ground state is $\Sigma_g$; the vibrational symmetry of the $v^+ = (101)$ level is $\Sigma_u$ and the closest electronic state that has $\Sigma_u$ symmetry is the $B^2\Sigma_u^+$. The direct product of the vibrational and electronic wavefunctions has $\Sigma_g$ symmetry.
conclusion – i.e., that the data are consistent with the Herzberg-Teller mechanism for this case – is something that we wish to test for other systems and over a broader energy range. We will see that other explanations can emerge to explain similar observations.

Figure 2.2 Photoelectron asymmetry parameters from Roy et al. obtained over the energy range 20 to 28.5 eV for the vibrational ground state (000), the forbidden vibration (101), and the $B_2^2\Sigma_u^+$ state. The (101) does not track the (000) but does track the $B_2^2\Sigma_u^+$ asymmetry parameter. This is consistent with the Herzberg-Teller mechanism for the appearance of the forbidden transition. The line through the (101) data is hand drawn to guide the eye.

2.5 Photoelectron Mediated Vibronic Interactions

Recently, experimental and theoretical work have shown that mechanisms other than Herzberg-Teller coupling can be responsible for inducing forbidden transitions. In fact, the experimental results which I present in subsequent chapters motivated additional theoretical work to demonstrate that qualitatively new mechanisms
can be responsible for the occurrence of nominally forbidden vibrational excitations in photoionization transitions. The full theoretical development was developed by Lucchese \textsuperscript{5,6,35} and will now be discussed.

If inclusion of the vibrational part of the Born-Oppenheimer molecular wavefunction leads to a nonzero dipole matrix element, then the nominally forbidden transition can occur. This is referred to as type (a) vibronic interaction, and is a non-Franck-Condon effect that involves molecular vibrations that lower the symmetry of the molecule. In the linear triatomic systems studied in this work, it is possible to observe excitation of forbidden asymmetric and bending modes. The type (a) vibronic interaction was identified in a prior study on the excitation of a single quantum of bending bending.\textsuperscript{5,6} The importance of the type (a) vibronic mechanism is that it is intrachannel in nature and no oscillator strength is “stolen” from alternate electronic manifolds.

The calculations for the vibronic matrix elements are analogous to calculations for a final state bound state electron that were described earlier. However, the details are more complex than for bound-bound electronic transitions. This is because the calculations must consider ejection of photoelectrons in specific directions (denoted by the wavevector, $\hat{k}$), and one must average over all possible photoelectron ejection directions as well as molecular orientations relative to the polarization vector. Let’s first consider a simple one-dimensional case, such as an asymmetric stretch. The intensity of a photoelectron transition is determined by scattering matrix elements such as the one given in the equation below.

$$f_{(f\rightarrow i)}(\hat{k}, \hat{n}) = \left\langle \chi_{vi}^{(i)}(q) \left| f(\hat{k}, \hat{n}, q) \right| \chi_{vf}^{(f)}(q) \right\rangle_q$$  \hspace{1cm} (2.18)
The inversion of the vibrational wave functions $\chi$ have definite symmetry with respect to the parity operator $q$ and $f_i(f \leftarrow i) (k, n)$ is an electronic amplitude; finally the term $f(k, n, q)$ is an electronic matrix element. Now, we expand the electronic amplitude in the vibrational coordinate $q$ and retain the first two terms:

$$f(k, n) = F_0(k, n) + qF_1(k, n) \quad (2.19)$$

where $F_0$ and $F_1$ are orthogonal to each other when an integration over all directions $\hat{k}$ and $\hat{n}$ is performed. It is essential that these distributions are orthogonal in (2.19), which therefore implies that the total cross section averaged over all orientations will be an even function of $q$. Substituting equation (2.19) into equation (2.18) now yields:

$$f_{(i \rightarrow f)}(k, n) = F_0(k, n) \langle \chi_{v_i}^{(i)}(q) \chi_{v_f}^{(f)}(q) \rangle + F_1(k, n) \langle \chi_{v_i}^{(i)}(q) q \chi_{v_f}^{(f)}(q) \rangle \quad (2.20)$$

Franck-Condon selection rules come from the $F_0$ term; allowed transitions have $v_f - v_i = 2n$. The second term leads to transitions where $v_f - v_i = 2n+1$, i.e., nominally forbidden transitions. They arise because the dipole amplitudes are allowed to vary with the vibrations corresponding to the non-totally symmetric modes. The essential point in this development is that the transition amplitudes that lead to the non-Franck-Condon transitions are odd functions of $q$, as is clear from equation (2.20).

Next, I expand this argument to the two-dimensional case, such as bending motions for linear $A \hat{B} \hat{C}$ molecules. Similar equations can be written; $(x, y)$ will be used for the Cartesian system and $(q, \gamma)$ in polar coordinates for the bending coordinates. Then equation (2.18) becomes

$$f_{(i \rightarrow f)}(k, n) = \langle \chi_{v_i}^{(i)}(x) \chi_{v_f}^{(f)}(y) \rangle f(k, n, x, y) \langle \chi_{v_i}^{(i)}(x) \chi_{v_f}^{(f)}(y) \rangle \quad (2.21)$$

Expanding in terms of the vibrational coordinates gives
\[ f(\hat{k}, \hat{n}, x, y) = F_0(\hat{k}, \hat{n}) + xF_x(\hat{k}, \hat{n}) + yF_y(\hat{k}, \hat{n}) \]  \hspace{1cm} (2.22)

and substituting into (2.21)

\[ f_{i \rightarrow f}(\hat{k}, \hat{n}) = F_0(\hat{k}, \hat{n}) \langle \chi_{\nu i}^{(i)}(x) \mid \chi_{\nu f}^{(f)}(x) \rangle_x \langle \chi_{\nu i}^{(i)}(y) \mid \chi_{\nu f}^{(f)}(y) \rangle_y \]

\[ + F_x(\hat{k}, \hat{n}) \langle \chi_{\nu i}^{(i)}(x) \mid \chi_{\nu f}^{(f)}(x) \rangle_x \langle \chi_{\nu i}^{(i)}(y) \mid \chi_{\nu f}^{(f)}(y) \rangle_y \]

\[ + F_y(\hat{k}, \hat{n}) \langle \chi_{\nu i}^{(i)}(x) \mid \chi_{\nu f}^{(f)}(x) \rangle_x \langle \chi_{\nu i}^{(i)}(y) \mid \chi_{\nu f}^{(f)}(y) \rangle_y \]  \hspace{1cm} (2.23)

These can also be written in polar coordinates to give

\[ f_{i \rightarrow f}(\hat{k}, \hat{n}) = \langle \chi_{\nu i, q}^{(i)}(q) \mid f(\hat{k}, \hat{n}, \hat{q}, \gamma) \rangle \chi_{\nu f, q}^{(f)}(q) \rangle \]  \hspace{1cm} (2.24)

repeating the expansion for the transition amplitude gives:

\[ f(\hat{k}, \hat{n}, q, \gamma) = F_0(\hat{k}, \hat{n}) + qe^{i\gamma} F_x(\hat{k}, \hat{n}) + qe^{-i\gamma} F_y(\hat{k}, \hat{n}) \]  \hspace{1cm} (2.25)

Analogous to the one-dimensional case the F functions, where \( F_1 = (F_x + F_y)/2 \) and \( F_{-1} = (F_x - F_y)/2 \) must be orthogonal (to \( F_0 \) or each other). The transition amplitude is now

\[ f_{i \rightarrow f}(\hat{k}, \hat{n}) = F_0(\hat{k}, \hat{n}) \langle \chi_{\nu i, l}^{(i)}(q) \mid \chi_{\nu f, l}^{(f)}(q) \rangle \delta_{l, l'} \]

\[ + F_1(\hat{k}, \hat{n}) \langle \chi_{\nu i, l}^{(i)}(q) \mid \chi_{\nu f, l}^{(f)}(q) \rangle \delta_{l, l'} \]

\[ + F_{-1}(\hat{k}, \hat{n}) \langle \chi_{\nu i, l}^{(i)}(q) \mid \chi_{\nu f, l}^{(f)}(q) \rangle \delta_{l, l'} \]  \hspace{1cm} (2.26)

The first term again leads to the Franck-Condon transitions, and the non-Franck-Condon forbidden transitions arise from the \( F_1 \) and \( F_{-1} \) terms. The symmetry in the two-dimensional case is controlled by the motion about the \( z \)-axis, which the Kronecker-\( \delta \)'s indicate in equation (2.26). Due to the equivalence of (2.20) and (2.26), it can be clearly observed that vibronic transitions are still determined by the symmetry of the one-dimensional bending modes.
Figure 2.3 A simplified view of intrachannel photoelectron mediated mechanism

The most important part of this development is that it invokes no interchannel coupling, either explicitly or implicitly. The outgoing photoelectron is now responsible for the intensity in the excitation of non-totally symmetric vibrations. A simple picture of photoelectron mediated vibronic coupling is shown in figure 2.3. However, there needs to be some mechanism that makes the electronic matrix element depend strongly on
changes to molecular geometry, i.e., the $F_{st0}$ terms in Eq.(2.20) and (2.26). The source of this dependence, i.e., the basis for the Franck-Condon breakdown, is discussed in the following section.

2.6 Franck-Condon Breakdown

Franck-Condon breakdown in photoionization arises from a strong $R$ or $Q$ dependence in equation (2.8), i.e., so equation (2.9) does not follow. Therefore, a fixed value for the electronic matrix element (i.e., independent of $Q$) is not valid and its variation with geometry must be considered. There are many examples of non-Franck-Condon behavior in the literature originating from above threshold features such as shape resonances, Cooper minima, and autoionization. A brief discussion of these three phenomena follows.

2.6.1 Shape Resonances

Shape resonances are ubiquitous single-electron phenomena that occur in ionization continua. Dehmer gave the first explanation of shape resonance behavior. A shape resonance is a quasi-bound state, where the outgoing photoelectron is temporarily trapped by a barrier, which is usually centrifugal in nature. The photoelectron eventually tunnels out of the barrier, as the energy of the electron is positive with respect to the vacuum level. The term “shape resonance” is derived from the nature of the phenomenon, i.e., the trapping of the continuum electron is strongly sensitive to the shape of the potential experienced by the continuum photoelectron. The shape of the barrier depends on the details of the inner and outer wells of a localized potential. A quasibound state can be formed inside a potential barrier on the perimeter of the molecule, and the photoelectron density will be enhanced in the region of the molecular core. This
localization leads to resonance features in photoionization processes. In particular, because of the localization, the dipole matrix element is enhanced in the vicinity of a shape resonance, so the partial photoionization cross section goes through a maximum, and this can be quite pronounced. Other effects are also observed, such as excursions in the photoelectron angular distributions.\textsuperscript{9,26,37} One of the primary issues that this thesis will be helpful in addressing is how the electron becomes localized in a polyatomic system.

Shape resonances frequently result in deviations from Franck-Condon behavior. There are two ways of rationalizing why such breakdowns occur. First, because the time scale of the electron escape becomes comparable to the period of vibrational motion, it is possible for the electronic and vibrational motions to become entangled, invalidating the assumption of Eq. 2.8. An alternative, but equivalent view, is that the effectiveness of the photoelectron trapping depends sensitively on the shape of the potential experienced by the photoelectron. This potential barrier depends on the molecular geometry, as shown by a variety of calculational studies.\textsuperscript{9,36,38-40} Regardless of the interpretation, there is a strong likelihood that there will be “communication” between electronic and nuclear degrees of freedom, i.e., Franck-Condon breakdown.

The barrier the electron feels in photoionization can be represented schematically in a one-dimensional picture.\textsuperscript{9,24,41} The inner part of the potential well is formed by partial screening in the molecular core and is therefore highly anisotropic and overlaps much of the molecular charge distribution. The centrifugal barrier comes from competition between repulsive centrifugal forces and attractive electrostatic forces that usually reside on the periphery of the molecular charge distribution.\textsuperscript{9,26} The periphery of
the molecule is where centrifugal forces can compete with electrostatic forces. The barrier (cf. figure 2.4) is like a simple one-dimensional barrier in introductory quantum mechanics. Competition between the Coulomb potential \(\approx - r^{-1}\) and centrifugal repulsion terms \(\approx + r^{-2}\) give rise to this barrier. The horizontal axis is the distance of the photoelectron from the center of the molecule. (Clearly, this will be anisotropic in a real system, and this level of complexity cannot be represented in the cartoon view given here.) There are three different continuum energies shown in Fig. 2.4 to demonstrate the effect of the barrier. When the photoelectron has kinetic energy less than that of the resonance, and the inner well of the potential doesn’t support a bound state, and the photoelectron can tunnel out of the barrier. At resonance conditions, a quasibound bound state can be supported in the inner well, and the amplitude of the wave function is greatly enhanced. The wave function decays exponentially in the barrier region; if the barrier were extended to \(r \to \infty\), a true bound state would lie near this energy. The electron is essentially bound at this resonance. Finally, for the energy of the electron greater than the resonance energy, the electron is an eigenfunction of the outer potential and is no longer a bound state.

The breakdown of the Franck-Condon approximation comes about from the quasibound character of shape resonance features. The localization induced by a shape resonance has consequences for photoionization, and the polyatomic implications are a significant part of this dissertation. The barrier – and therefore the energy and lifetime of the resonance – are sensitive to changes in the molecular geometry.
In diatomic molecules, the effects of nuclear motion on shape resonances have been well studied. Figure 2.5 are calculated results for the $\sigma_u$ shape resonance in the $3\sigma_g \rightarrow k\sigma_u$ ionization channel of $N_2$. The data in the left frame are cross sections
(σ) for the $3σ_g$ ($v_i = 0$) level of N$_2$ photoionization for different fixed-R calculations. In the right frame are the vibrationally resolved final state cross sections for the $v^+ = 0$-2 levels. The dashed lines in the left hand frame are the fixed-R results and the solid line in the left hand frame is the R-averaged curve (equivalent to vibrationally unresolved data). Non-Franck-Condon behavior arises from the quasibound nature of shape resonances, the barriers reside primarily on the periphery of the molecular framework. Changes in the internuclear separation, R, will affect the trapping of the electron, and hence, affect the resonance. Small variations in R effectively shift the resonance. The effective potential for the $σ_u$ wave function is more attractive at large values of R, and the shape resonance shifts to lower kinetic energy. It also becomes higher and narrower. For smaller values of R, the effective potential is more repulsive and the resonance is shifted to higher energies and is weakened. This example clearly shows that the resonance positions, strengths, and widths are sensitive to the internuclear separation, R. As the bond length is increased, the resonance is shifted to lower energy and it becomes narrower and more intense. The opposite happens as the bond length is shortened. An implication of this figure is that one can investigate the underlying photoionization dynamics of shape resonances by investigating the details of how non-Franck-Condon behavior are manifested. The effects of shape resonances for diatomic systems have been studied in great detail and with high precision, both experimentally and theoretically. However, it has not been possible to bring the same level of understanding to polyatomic systems, owing to technical constraints that have existed in the past. This is a primary focus of my thesis research, i.e., to understand how a continuum electron becomes localized in polyatomic systems undergoing shape resonant photoionization. It will be seen that dramatic and
unanticipated affects emerge naturally from such studies, and that they provide a window into previously unexplored aspects of molecular electronic spectroscopy.

Figure 2.5 The frame on the left shows calculated cross sections for the $3\sigma_g$ ($v_f = 0$) level of N$_2$ photoionization. The dashed lines are the fixed-R calculations and the solid line is the R-averaged calculation. The frame on the right shows the R-weighted results for the ionic vibrational levels $v_f = 0-2$. These results are from calculations described in reference. 25

2.6.2 Cooper Minima

Photoionization processes can also be greatly affected by Cooper minima. 31,32,45 The cross sections, asymmetry parameters, and other dynamical variables are known to be influenced by the presence of Cooper minima. 32,45 So, it is appropriate to review what gives rise to such phenomena, and how they might be expected to influence the results observed here. Indeed, future studies on systems identified with theoretical calculations could extend the scope of the current work to encompass effects of Cooper minima.
The historical experiments which revealed the presence of Cooper minima were cross section measurements on alkali metals, where broad minima were observed as a function of energy.\textsuperscript{46} The explanation was that there was cancellation in the radial part of the dipole matrix element that resulted from opposite contributions from the positive and negative lobes of the initial state wavefunction when the photoelectron energy is tuned to a specific value. The explanation for this phenomenon was originally provided by J.W. Cooper for atomic systems.\textsuperscript{31} The formulation he used was to separate the wave function into radial and angular parts, and integrate over the angular coordinates. Then, one is left with the radial dipole matrix element, which can be expressed as

\[
R_{l\pm}(\varepsilon) = \langle u_{l,\pm}(r) | r | u_{n}(r) \rangle \quad (2.27),
\]

where \(u_{nl}(r)\) and \(u_{l,\pm}(r)\) are electronic wave equations of the initial and final states. Because there can be radial nodes in the initial state wavefunctions (e.g., for s orbitals), this quantity can change sign when the photoelectron energy is adjusted so that the r-weighted overlap integral has opposing contributions from the positive and negative lobes of the initial state wavefunction. The change in sign results in the dipole matrix element going through a zero.

It was shown by Cooper that this cancellation was a general result.\textsuperscript{31} Cooper studied the photoionization cross sections of rare gases and metals.\textsuperscript{31,47} To understand what he found, we will consider the examples of the photoionization of neon and argon from their outermost np valence orbitals.\textsuperscript{31,48} The Ne (2p) and Ar (3p) radial wave functions and the d-wave radial wave functions for near-threshold ionization are plotted in figure 2.6. It is clear that the final state d-wave matrix element for neon is positive while for argon it is negative. Wavefunctions for argon have opposite signs in the region
of the overlap. Increasing the photoelectron energy ($\varepsilon$), the nodes of the d-wave get drawn toward the origin, and this negative lobe of the photoelectron can now have appreciable positive contributions to the radial matrix element.

Figure 2.6 The outer subshell radial wavefunctions and d-waves at zero kinetic energy for Ne(2p) and Ar(3p) from reference. 31

The $R_{l+1}$ integral is plotted as a function of the photoelectron kinetic energy for Ne and Ar in Fig. 2.7. As the photoionization of argon at higher energy shows, the negative lobe of the de Broglie wave cancels out all the positive contribution of the d-wave in the dipole matrix element. The result is a zero. In the neon case there is no negative contribution and the dipole matrix element is positive over the whole range.
studied. For neon and argon, the d-waves are similar functions, yet the initial states are quite different, $2p$ and $3p$. This demonstrates the conditions required to have Cooper Minima. Namely, for atomic species, negative lobes in the initial state wave function leads to a change in sign in the radial matrix elements, which in turn leads to complete cancellation of the positive dipole matrix elements as a function of the excitation energy. When more excitation channels are open, the Cooper “zero” becomes a Cooper “minimum” because other channels can contribute to the cross section which do not have this cancellation effect.

![Figure 2.7 matrix elements for the $p \rightarrow d$ transitions in Ne and Ar, from reference.](image)

Cooper minima can modulate oscillator strength and affect photoelectron angular distributions over a broad range of photon energies. This has been observed for both atoms and molecules. More recently, though, there has been work on determination of molecular vibrational branching ratios over a broad range of photon energies for $2\sigma^1_u$ photoionization of N$_2$. It was determined for that case that Cooper minima could
exhibit significant shifts with changes in internuclear separation. As a result of the sensitivity of the electronic component to changes in nuclear coordinates, Franck-Condon breakdown was observed. Specifically, it was determined that the \( v^+ = 1/v^+ = 0 \) and the \( v^+ = 2/v^+ = 0 \) branching ratios showed unanticipated excursions over a very broad range of energy (ca. 80-100 eV). So, it is incumbent on us, as we search for molecular influences on the photoelectron behavior in polyatomic systems, to investigate possible influence of Cooper minima on the vibrationally resolved aspects of the scattering process.

2.6.3 Autoionization

Photoionization can be sensitive to autoionization \(^{28}\), which differs from a shape resonance in that it is a multichannel, indirect process. So far, the discussion has only focused on direct ionization processes. Indirect ionization processes can compete with direct ionization. In fact, autoionization phenomena have been studied much more extensively than shape resonances. These features can greatly affect the distribution of energy in the residual photoion, and hence, the photoelectron spectra when the photon energy is resonant with an autoionizing level. Autoionization affects the cross section, i.e., it affects the measured spectrum. \(^{52}\) The outgoing photoelectron can contain information about the initial and final state wave functions, as well as the intermediate (gateway) state that feeds into the ionization continuum. The following will focus on electronic and vibrational autoionization. Electronic autoionization is typically observed when an inner valence electron is excited to a Rydberg level, and the resulting Rydberg state has sufficient energy to ionize the molecule (i.e., lies above the ionization threshold for ionizing a less tightly bound electron). For this level to produce the
photoion/photoelectron pair, the Rydberg electron must “collide” a less tightly bound
valence electron, resulting in the Rydberg electron dropping into the level from which it
was excited, and in so doing, provide sufficient energy for the less tightly bound electron
to escape into the continuum. Clearly, this is not a direct process; more specifically, it is a
two-electron process involving the $r_{12}^{-1}$ matrix element. Autoionization resonances are
localized close to the ionization threshold and are typically less than 0.25 eV in width,
and can be as narrow as a few tens or hundreds of microvolts. For these reasons, they
will not be a major focus of the current work, but it must be anticipated that non-Franck-
Condon effects can also result from these processes as well.
CHAPTER THREE: EXPERIMENTAL

3.1 Introduction to Experimental Scheme

My work exploited two different and complementary experimental schemes. First, I used high-resolution photoelectron spectroscopy (PES) coupled to undulator-based synchrotron radiation excitation. Second, I performed dispersed fluorescence measurements using excitation radiation from a bending-magnet synchrotron radiation source. Most of the measurements reported here used the photoelectron spectroscopy strategy. For both methods, the strategy is as follows. By changing the photon energy, the photoelectron kinetic energy can be adjusted precisely, e.g., it can be tuned through the energy of a continuum feature of interest (typically a shape resonance). Because both methods are amenable to wide-ranging studies, they permit us to study slowly varying aspects of the photoionization process. The experimental techniques are different but both allow us to resolve vibrational motions selectively and with high precision. PES and dispersed fluorescence end up being complementary for my studies. This chapter will explain the experimental philosophy of mode-specific molecular photoionization over a broad range of excitation energies. I will discuss synchrotron radiation, photoelectron spectroscopy and dispersed fluorescence.

3.2 Molecular Photoionization Studies

The absorption of light can induce different physical processes, depending on the photon energy and initial state of the target molecule. One of the simplest processes is photoionization: a photon of sufficient energy collides with a molecule and produces a photoion and a photoelectron. If the photon has sufficient energy, inner valence electrons can be removed from the target molecule, which results in the production of an
electronically excited state. Such a state can give up its electronic energy via fragmentation or fluorescence. Some of the systems that I studied decayed (at least in part) radiatively, i.e., via fluorescence

\[ M + h\nu \rightarrow M^{+*} + e^- \]
\[ \downarrow \]
\[ M^+ + h\nu^* \quad (3.1). \]

The fluorescence of the photoion contains information about energy that was deposited in the ion as the outgoing photoelectron leaves the molecule. Alternatively, one can measure the photoelectron spectrum to understand the internal energy distribution for the photoion. Looking a figure 3.1 we can start to learn some the advantages and disadvantages of both PES and fluorescence as applied to photoionization.

Figure 3.1 is a schematic comparison of PES and dispersed fluorescence. The main disadvantage of the photoelectron method is that any energy spread in the incident photon source is directly transferred to the photoelectron. It is straightforward to see this. The energy conservation for ejection of a photoelectron is given by the equation \( E_k = h\nu - E_b \). Differentiation of this equation implies that \( \delta E_k = \delta(h\nu) \), as \( E_b \) is a constant. In other words, the photon bandwidth is the lower limit to the uncertainty in the photoelectron energy resolution. For many synchrotron radiation experiments at higher energies, it is not uncommon for the photon bandwidth to exceed 100 meV, and this uncertainty will propagate to the uncertainty in the kinetic energy imparted to the outgoing photoelectron. If one wishes to study low frequency modes with vibrational spacings less than 100 meV, it is necessary to use sources whose specifications exceed this limitation, or to use alternative methods. In this thesis, both approaches were used.
In fluorescence, the resolution for the fluorescent radiation is not determined by the resolution of the ionization source. The resolution is dependent on the instrumental bandwidth of the fluorescence monochromator. So, dispersed fluorescence was appropriate for studies of the systems that decayed radiatively, while most of the systems were investigated using photoelectron spectroscopy by exploiting the capabilities of third generation synchrotron radiation sources. These can produce high brightness and high resolution over a broad range of energies. In the following sections I will discuss the experimental philosophy for PES and fluorescence.

Figure 3.1 Comparison of photoelectron spectroscopy and dispersed fluorescence; note the independence of dispersed fluorescence resolution on the excitation bandwidth. The measurement of the photoelectron kinetic energy is dependent on the excitation bandwidth.
3.2.1 Photoelectron Spectroscopy and Molecular Photoionization

Photoelectron spectroscopy is performed by illuminating a target atom, molecule or surface with monochromatic radiation that is above the ionization threshold of the system of interest. The electrons that are ejected from the target system have different kinetic energies depending how strongly bound the electrons are in the system. The intensities and kinetic energy of the ejected photoelectrons can be measured. This a measurement of the electronic environment of the target system. Photoelectron spectroscopy’s main advantage is that is a direct measurement of the electron and therefore a direct measurement of the scattering event. The method is more widely applicable, as it does not depend on having a molecular ion state that decays radiatively as is needed for fluorescence. It is always clear that the photoelectron band under investigation corresponds to creation of a specific electronic state of the ion, i.e., the process generating the photoelectron is always easily identifiable based on energy constraints (as opposed to fluorescence, where cascading and secondary processes can introduce subtle artifacts). This makes the analysis of vibrational branching ratios straightforward. This is not the case for fluorescence and will be discussed in the next section. The main disadvantage of photoelectron spectroscopy is that the detection bandwidth is coupled to the excitation bandwidth. This can make it very challenging to obtain high-resolution photoelectron spectra over a wide range of photoelectron kinetic energies. Historically, high-resolution photoelectron spectra have been performed with resonance lamps and lasers. Recently, Zero Electron Kinetic Energy-Pulsed Field Ionization (ZEKE-PFI) has generated very highly resolved data (ca. 0.05 meV), but by definition, these experiments are limited to threshold studies. In the
past, there has been significant molecular photoelectron work done with synchrotron radiation, but this work has been limited to vibrationally unresolved studies or to systems with very high vibrational frequencies (e.g., second-row diatomic samples such as N₂ and CO). This limitation has been a result of the broad excitation bandwidth characteristic of older synchrotron radiation sources. With the advent of insertion devices specifically, undulators ⁶⁴, it is now possible to have high brightness while maintaining a sufficiently narrow excitation bandwidth (≈ 10 meV) to study low frequency vibrations of polyatomic systems, such as the CO₂, CS₂ and N₂O studies described in subsequent chapters. Spectral brightness, $b$, is defined as

$$b = \frac{dn_{0.1\%}(x,y,\theta, \Phi, h\nu)}{idxdyd\Omega dt} \quad (3.2)$$

where $dn_{0.1\%}$ is the number of photons emitted by the area $dxdy$ of the source, located at a point $(x,y)$, over the bandwidth $\Delta h\nu = 0.1\% h\nu$, centered at a photon energy of $h\nu$, over the solid angle $d\Omega$ in a direction defined by the two angles $\Phi$ and $\theta$, in the time interval $dt$. In other words, the spectral brightness is an emission in a 0.1% fractional bandwidth at $h\nu$, normalized for time, source area, solid angle and the ring current. The brightness of the undulator used for these experiments is approximately $10^{18}$ photons/mm² mrad²/sec 0.1% BW. To see why this undulator-based synchrotron source is important in my studies, consider that the energy separation between the $v^+ = (000)$ and the $v^+ = (010)$ levels for the CO₂⁺($C^2\Sigma^+_g$) state is 76 meV, so vibrationally resolved photoelectron spectra are accessible only using undulator based synchrotron radiation. This is because second generation synchrotron radiation sources cannot generate the high brightness radiation required for simultaneously generating high flux radiation and high resolution.
On the other hand, second generation sources are well-suited for the dispersed fluorescence measurements described below.

### 3.2.2 Dispersed Fluorescence and Molecular Photoionization

Dispersed fluorescence experiments make use of a simple experimental trick, and this is described in detail elsewhere. The strategy is summarized briefly here. By detecting the fluorescence from a photoion of interest, the detection bandwidth is not limited by the excitation bandwidth. This is ideal for studying the photoionization far from threshold, provided that the molecular ion of interest has a substantial quantum yield for fluorescence. The only constraint on the excitation bandwidth is that it must be narrower than any excitation features of interest. Typically, shape resonances are on the order of 10 eV wide and Cooper minima effects extend over even broader ranges, so bandwidths of 0.5 eV are more than sufficient for the studies that I will describe. The key point is that these experiments utilize the most flux, and are ideally suitable for experiments at second generation synchrotron radiation sources. Vibrationally resolved spectra are straightforward to measure with dispersed fluorescence. It also possible to get rotationally resolved spectra tens and hundreds of eV past the ionization threshold, although this is not the topic of my dissertation research. Rotationally resolved data over a broad energy range are currently not accessible using PES methods.

A complication for the dispersed fluorescence measurements is that the transition undergoing fluorescence might result from processes not of direct interest. For example, an excited vibrational level of the ion undergoing fluorescence can be formed either from direct ionization of the ground state neutral, or from hot-band ionization of a vibrationally excited neutral level. Hence the parentage is not always well known (e.g., cascading
transitions from higher electronic states can produce the state under investigation, and complicate the analysis commensurately). This complicates the analysis of intensity branching ratios that are generated via fluorescence measurements.\textsuperscript{5,6,34} Also, different excited levels undergoing fluorescence might have different predissociation rates, which are not well determined.\textsuperscript{55,56} To get a true vibrational branching ratio from fluorescence, the ratio of fluorescence intensity must be corrected for such differences in order to generate a true vibrational branching ratio. The relationship between the intensity ratio and the vibrational branching ratio is given by:

$$\frac{\sigma_{\nu_1^+}}{\sigma_{\nu_2^+}} = \frac{I_{\nu_1^+}}{I_{\nu_2^+}} \cdot \frac{q_{\nu_1^+}}{q_{\nu_2^+}} \cdot \left(\frac{v_{\nu_1^+}}{v_{\nu_2^+}}\right)^3 \cdot \frac{\Phi_{\nu_1^+}}{\Phi_{\nu_2^+}} \quad (3.3)$$

Here $I_{\nu^+}, q_{\nu^+}, v_{\nu^+}, \Phi_{\nu^+}$ denote the intensity, the Franck-Condon Factor, the transition frequency, and the fluorescence quantum yield, respectively. We will now turn our attention to characteristics of synchrotron radiation. As alluded to previously, the “generation” of a synchrotron radiation source has implications on which experiments are possible.

\textbf{3.3 Synchrotron Radiation}

Synchrotron radiation was initially just an unwanted byproduct of accelerator physics experiments, because the energy lost to radiative emissions of the stored beams had to be made up using advanced power injection schemes (typically RF cavities in the accelerator rings). In the late 1950 and early 1960 groups began utilizing synchrotrons for spectroscopic applications in the far ultraviolet region that will be defined as $> 20$ eV, where alternative sources of continuously tunable radiation with high flux were not (and still are not) available. First generation sources were accelerator rings designed for other
purposes (typically particle physics collision experiments) that had beamlines attached. The accelerators were not designed or optimized for synchrotron radiation experiments. In fact, the mode of operation of these early synchrotron radiation experiments was referred to as “parasitic operation.” Second generation sources were dedicated to the production of synchrotron radiation. The radiation was emitted from the sectors of the storage rings where the dipole magnets steered the electron beams to form the ring. This radiation is referred to as “bending magnet” radiation, and second generation synchrotron radiation sources used this type of radiation to perform the various experiments. Finally, third generation sources were designed with long straight sections. In the straight sections insertion devices are placed. These devices steer the stored electron beam so that it undergoes tight radius turns (i.e., wiggle) or undulates, and the characteristics of the radiation pattern (energetically and geometrically) are markedly different than is the case from bending magnet sources. In particular, the flux from undulators into a small solid angle is much greater for a third generation source than a second generation source. They also have a small photon beam size relative to second generation sources. Also, undulator insertion devices utilize constructive interference to produce more of the flux in a more limited range of the spectrum, which is desirable for highly differential experiments such as the ones I will describe. My work has utilized both second and third generation sources, although the majority of the experiments that I performed used the third generation facility at the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory.

My photoionization experiments \(^{64}\) require continuously tunable vacuum ultraviolet (VUV) and soft X-ray photons in the energy range of \(15 \leq h\nu_{\text{exc}} \leq 300 \text{ eV}\).
Synchrotron storage rings are the only high intensity source of continuously tunable VUV and soft X-ray radiation. Synchrotron radiation is electromagnetic radiation emitted by electrons moving at velocities close to the speed of light along a curved trajectory. For bending magnet sectors, a typical radius of curvature is on the order of several meters. The electrons emit radiation over a broad range of energies form the microwave region to the hard X-ray region of the electromagnetic spectrum.

The universal curve for the CAMD storage ring is shown in figure 3.2. The plot shows the photon flux versus the photon energy. The curve is characterized by the critical energy, $\hbar \nu_c$ which is defined by

$$\nu_c = \frac{3hc\gamma^3}{4\pi\rho}$$

(3.4).

$$\gamma = \frac{E}{(m_0c)^2}, \quad \rho = CE / B$$ where $E$ is the electron energy in GeV, $B$ is the magnetic field of the dipole bending magnets in Tesla, and $C$ is a constant. The critical energy is a measure describing the usable range of a synchrotron radiation source. Half the power emitted is above the critical energy and half is below. A typical estimate is that there is usable flux at photon energies that are four times the critical energy. The critical energy for bending magnet radiation at CAMD is 1.66 keV for 1.3 GeV beam energy. This provides good flux for the experiments done over the energy range of interest for these experiments.

These experiments were performed at the third generation synchrotron source the Advanced Light Source (ALS) and a second generation synchrotron source Center for Advanced Microstructures and Devices, (CAMD).
Figure 3.2 Plot of the photon flux versus the photon energy at CAMD.\textsuperscript{66,67}

The experiments that were done at CAMD\textsuperscript{66,67} utilized synchrotron radiation from bending magnets. Bending magnets are the most common sources of synchrotron radiation. Bending magnets have many characteristics that make them ideal for a host of experiments. They produce an extremely wide range of photon energies from the infrared to hard X-rays. The photons are collimated over a narrow range of vertical angles and have high intensity. The polarization of the radiation is linear in the plane of the ring and elliptical above and below the plane. There is time structure, with the photon pulse width being some fraction of a nanosecond with the interval between pulses being on the order of a few nanoseconds. However, these experiments I will describe used the incident radiation as a cw source. Typical fluxes incident on the target samples in my studies were on the order of $10^{12}$ photons/sec. In the case of the experiments at CAMD,
the bandwidth was very wide (~0.4 eV), while the incident bandwidth was approximately 0.01 eV for the experiments performed at the ALS.

3.3.1 Insertion Devices

In third generation synchrotron sources (such as the ALS 68) the storage rings are specifically designed for insertion devices such as wigglers and undulators. Insertion devices “wiggle” the electron trajectories in the straight sections of the synchrotron. The deviation of the electrons trajectory form an otherwise straight trajectory that will result in the emission synchrotron radiation.

The simplest type of insertion device is a wiggler, or wavelength shifter. The electron orbit is forced through a trajectory with a small radius of curvature. The radiation produced is similar to that of a bending magnet. The magnetic fields used in a wavelength shifter can be much stronger than that of a bending magnet. As a result the useable spectrum is shifted to higher photon energies. Wigglers were not used in this study.

An Undulator was used in this study. An undulator extends the ideas used for a wiggler. This is accomplished by a periodic array of magnets to produce a series of oscillations for the electrons from otherwise straight trajectories. The way to picture this is an array of magnets whose fields alternate between parallel and antiparallel to each other. Figure 3.3 shows a very simple “cartoon” of how an undulator functions. The result is oscillations all in the same plane that is perpendicular to the field axis. Electrons whose trajectories are wiggled emit synchrotron radiation. They emit radiation that is concentrated along the axis of the insertion device. If interference effects are ignored the spectrum of radiation is equivalent to that of several bending magnets, multiplied by two
times the number of periods of the magnetic array. However, interference can be very important for undulators. If the magnetic field used is weak and the number of oscillations (or periods) is large. The interference effects produces radiation centered around a fixed energy, and the spectrum is more concentrated over at one photon energy or centered over a few photon energy. The difference between normal wiggler, which have a universal curve similar to that of a bending magnet, “undulator” produce photons centered around a few energies. This high brightness at specific photon energies can be used for experiments that need high flux, narrow bandwidth, and tunability over a wide relatively range (though not the whole spectrum available from a bending magnet). To change the photon energy that is generated by an undulator, the spacing of the magnets in the array or the undulator gap is the only thing that needs to be changed.

Undulator Radiation

Figure 3.3 A simplified view of how an undulator produces a photon beam with high brightness and high resolution.

The insertion device used for these PES experiments Undulator 10 (U10) at the ALS. It employs a 4.5 m long device with 10 cm period, which provides a very bright source of synchrotron radiation. The energy range of U10 is $17 \leq h\nu \leq 340$ eV. It is clear that in the energy range of interest for this research, undulator based radiation is ideal for obtaining a photon beam with high brightness and high resolution. U10’s photon flux in the range we are interested in is approximately $10^{13}$ photons/mm rad/sec/0.01% BW.
3.4 Beamlines

The main function of a beamline is to filter the broad synchrotron radiation spectrum, and transmit the (narrow) band of photon energies that is required for each experiment. For my experiments, the filtering was done with grating monochromators. Crystal monochromators are used for hard X-ray experiments.

Two beamlines at CAMD were used for the dispersed fluorescence studies, a plane grating monochromator (PGM) and a toroidal grating monochromator (TGM). The PGM has an energy range of $20 \text{ eV} \leq \hbar \nu_{\text{exc}} \leq 1000 \text{ eV}$. The PGM can be operated in several modes. Specifically the pre-mirror-grating combination can be operated in different modes. For my experiments, all the dispersed fluorescence spectra were acquired with the PGM operating in high throughput mode. For the beamline to run in high throughput mode, the grating is operated at the blaze angle (i.e., where the flux is highest, but the monochromator does not stay focused for the highest resolution possible). At energies less than 50 eV it was sometimes operated in higher order rejection mode, because higher order transmission can be significant. Specific pre-mirror angles are used for specific energy ranges to reject higher order radiation. Finally the PGM can be operated in high resolution or fixed focus mode. The high resolution mode matches the pre-mirror to the energy setting of the grating. The monochromator is always in focus and the result is the highest resolving power. Calibration of this beamline is done by photoemission with an Al L$_{\text{III}}$ edge. In these experiments, the monochromator operated with a bandwidth of $\Delta \hbar \nu_{\text{exc}} \approx 0.2 \text{ eV}$.

The 3m toroidal grating monochromator (TGM) was utilized in one study (CS$_2$ dispersed fluorescence). This TGM beamline has an energy range of $15 \text{ eV} \leq \hbar \nu_{\text{exc}} \leq 300$
eV and we operated it with an excitation bandwidth of $\Delta h\nu_{\text{exc}} \approx 0.5$ eV (i.e., slits wide open for highest flux). The energy is scanned by rotation of the grating. The TGM provides moderate resolution and good flux. The spectral range is limited by the angle of incidence of the radiation on the grating. One problem with this type of beamline is there is limited rejection of higher order radiation, so filters are required for rejection of higher order radiation.

For the high-resolution photoelectron spectroscopy experiments, I used the undulator beamline 10.0.1 at the ALS, which is described in detail elsewhere. The spectral range for this beamline is $17 \leq h\nu_{\text{exc}} \leq 340$ eV. This is an undulator beamline equipped with a spherical grating monochromator (SGM). My measurements used the 380 line/mm grating for measurements in the range from $20 \leq h\nu_{\text{exc}} \leq 50$ eV, and the 925 line/mm grating for the range $50 \leq h\nu_{\text{exc}} \leq 110$ eV. High quality spherical reflective optics focus the beam through the entrance slit of the monochromator. Rotation of the gratings is the only motion needed to change the wavelength, the exit slit traverses along the optical axis to keep the monochromator in focus as the grating is rotated. The excitation bandwidth was held constant at 10 meV for these studies, and the ability to work at this comparatively high resolution over a very broad energy range was a critical aspect of these studies.

### 3.5 High Resolution Photoelectron Spectroscopy

Photoelectron spectroscopy of molecules is a method that exploits the photoelectric effect to probe the electronic, vibrational, and geometric structure of molecular ions. Photons of sufficient energy to remove a bound electron strike a target molecule of interest. If the photon is absorbed, the excess energy is transferred into the
electron kinetic energy. The photoelectron can be energy analyzed. The effect relies on energy conservation, as noted earlier, i.e.,

\[ E_k = h\nu - E_b \] (3.5).

Where, \( E_k \) is the electron kinetic energy, \( h\nu \) is the photon energy and \( E_b \) is the binding energy of the electron.

While the photoelectric effect has been well known for approximately a century, photoelectron spectroscopy was not fully developed as a technique for analyzing electronic structure until the 1960’s by the groups of Siegbahn 71 and Turner and Price. 72 A simplified picture for atoms and molecules in the gas phase is shown in figure 3.4. The figure divides the atomic and molecular orbitals into core and valence orbitals or shells. In this schematic picture, each orbital is pictured as being nondegenerate and the systems are represented as closed shell systems. The energy of the orbitals is negative relative to the reference energy (free electrons). Valence or outer shell orbitals have a higher orbital energy relative to core or inner shell orbitals. When a monochromatic source of X-rays is used to eject core-shell electrons, the method is usually called X-ray Photoelectron Spectroscopy, XPS, or ESCA (Electron Spectroscopy for Chemical Analysis). When less energetic vacuum ultraviolet radiation is used, only the valence shell electrons are ejected, and the measurements are referred to as ultraviolet photoelectron spectroscopy, or UPS. All of the work presented in this dissertation employed UPS.
Figure 3.4 Processes in UPS and XPS

The schematic of the photoelectron energy analyzer is shown in figure 3.5, and is described in detail in ref. 70. This spectrometer chamber is installed as an endstation at beamline 10.0.1. Differential ion pumping is used to separate the spectrometer chamber from the beamline that must be maintained at ultrahigh vacuum. The chamber has 2 layers of µ-metal magnetic shielding to ensure that the electrons are not steered by stray magnetic fields. The electron spectrometer uses a gas cell on the beam axis to form the ionization region between the gas sample and the photon beam. The pressure in the chamber is roughly $5 \times 10^{-6}$ Torr. The photoelectrons are analyzed with a 200 mm hemispherical energy analyzer (Scienta model SES 200). The analyzer uses an eight-element electrostatic lens system to retard the photoelectrons and focus them into the analyzer. The analyzer can be rotated from 0° to 90° degrees to study angular distributions, although such measurements are not performed in my studies. The analyzer is placed at 54.7° angle respect to the photon polarization angle. This is the magic angle for photoelectron spectroscopy, is the angle at which the photoelectron intensities are
independent of detection angle and is used in these experiments so there is no need to correct for differences in photoelectron asymmetries. The analyzer is made of two concentric hemispherical conductors, and the relative voltages on the hemispheres and the electrostatic lens elements at the entrance of the electron spectrometer are used to transmit energy-selected photoelectrons to the detector. The analyzed electrons are detected with microchannel plates (MCP) with a phosphor screen behind the MCP stack. The radiation from the phosphor is detected with a CCD. The pass energy (the energy with which the electrons are allowed to pass through the analyzer) for these experiments was 2 and 5 eV. The exit slits widths were 0.04, 0.05, and 0.06 cm, and these experimental conditions correspond to analyzer resolutions of 2, 2.5, and 3 meV, respectively. For CO₂, the spectrum taken with $h\nu_{\text{exc}}$ 25 eV has an overall resolution of 12 meV. That is consistent with photon and photoelectron bandwidths. The photon bandwidth is 10 meV and the photoelectron bandwidth is 2 meV.

Figure 3.5 Schematic of photoelectron energy analyzer at ALS.
3.5.1 Asymmetry Parameters in Photoelectron Spectroscopy

Photoelectron scattering is anisotropic, i.e. photoelectrons are not emitted equally in all directions.\textsuperscript{28} Data taken with photoelectron spectroscopy therefore depend on the angle of the analyzer with respect to the polarization of the photon beam. The photoelectron angular distributions for photoionization of non-chiral, randomly oriented molecules with linearly polarized light can be characterized by the following equation.\textsuperscript{28}

\[
I(\theta) = \frac{\sigma}{4\pi} \left[ 1 + \frac{\beta}{2} (3\cos^2 \theta - 1) \right] \quad (3.6)
\]

Where \(\sigma\) is the total cross section integrated over all angles, \(\beta\) is the photoelectron asymmetry parameter, and \(\theta\) is the angle between the photon polarization and the detection axis (i.e., the photoelectron wavevector). \(\beta\) is the single parameter needed to describe the angular distribution, and can take values from \(-1 \leq \beta \leq 2\). Note that \(\beta=2,0,\) and \(-1\) correspond to \(\cos^2 \theta\), isotropic, and \(\sin^2 \theta\) angular distributions, respectively. In practice, most photoelectron \(\beta\) parameters are positive with values close to 2, but the angular dependence of the problem can be neglected if one performs experiments at the magic angle of 54.7°, where the second Legendre polynomial in \(\cos \theta\) goes to zero. The angle of 54.7 is with respect to the electric field vector.

3.5.2 Doppler Broadening in Photoelectron Spectroscopy

Doppler broadening is a major problem for synchrotron radiation-based high-resolution photoelectron experiments.\textsuperscript{73} In the experiments described in later chapters, Doppler broadening accounts for the loss of resolution at higher energies. As the kinetic energy of the electron is increased, the broadening increases. The thermal motion of the molecules affects the kinetic energy in Eq. (3.5). This can be seen using a simple model.
Suppose that all of the sample molecules are moving in random directions, have the
velocity $\varepsilon$, and that the electron velocity relative to the target molecules is defined as $t$.
Let $m$ = mass of the electron. The maximum observed electron energy would be when the
photoelectron is ejected in the same direction as of motion of the molecule and the
minimum when it is ejected in the opposite direction, therefore

$$E'_{\text{max}} = \frac{1}{2} m (\varepsilon + t)^2$$
$$E'_{\text{min}} = \frac{1}{2} m (\varepsilon - t)^2$$

(3.7).

The total broadening is $\Delta E' = 2 m t$, and the width (FWHM) of the electron
signal $\delta$ is equal to $\frac{\sqrt{2}}{2} \Delta E'$ and the most probable velocity of the molecules is

$t = (2kT/M)^{\frac{1}{2}}$. The FWHM is now given by

$$\delta = 2(mEkT/M)^{\frac{1}{2}}$$

(3.8),

where $k$ is the Boltzmann constant, $T$ is the temperature in Kelvin, $M$ is the mass of the
molecule in amu, and $E = \frac{1}{2} me^2$ in electron volts. This can be simplified to

$$\delta_{\text{doppler}} = 0.723 \sqrt{\frac{VT}{M}}$$

(3.9)

where $V$ is the kinetic energy of the electron in eV, $T$ is in Kelvin and $M$ is units of amu
and the Doppler broadening is in units of meV. As the kinetic energy of the outgoing
photoelectron is increased, the broadening increases (with a square root dependence).

It should be mentioned that the only parameter that one has experimental control
over (for a given molecule) is the temperature. The use of a skimmed molecular beam
expansion can cool the molecules to a few degrees Kelvin and then high-resolution
spectra can be obtained, even far from threshold. Doppler broadening was responsible for the loss of resolution in these photoelectron experiments. For CO$_2$, the Doppler broadening of a 10 eV electron at 293 K is 8.5 meV, for a 100 eV electron at 293 K the broadening is 27.0 meV. If the initial temperature of CO$_2$ can be reduced to 15 K (a readily achievable temperature in a supersonic beam), the Doppler broadening will be reduced to 1.8 meV for 10 eV photoelectron and 6.1 meV for a 100 eV photoelectron. Supersonic expansions were not employed in my studies, but they are obviously important for future work as the scope of the experimental program is increased to include more complicated molecules with even lower vibrational frequencies.

3.6 Dispersed Fluorescence Experimental Station

Dispersed fluorescence spectroscopy experiments are straightforward, both in practice and in concept. The experiment is performed by photoionizing molecules and studying the dispersed fluorescence spectra resulting from electronically excited ions that are produced. The basic idea is that the intensity of fluorescence emitted from a specific quantum level of an excited photoion is proportional the rate at which the level is produced (i.e., the partial photoionization cross section for that level). Thus, the information from a dispersed fluorescence spectrum is similar to that from a photoelectron spectrum, but there are subtle and important differences. An important advantage of dispersed fluorescence is that the excitation bandwidth is not coupled to the detection bandwidth. This allows highly resolved spectra to be taken over a very broad range without the requirement of narrow bandwidth excitation radiation. This is important when using synchrotron radiation where the excitation bandwidth can be quite broad. The reason why dispersed fluorescence experiments were not used for most of my
dissertation research is that many of the systems that I needed to study did not fluoresce, but decayed via nonradiative mechanisms.

Figure 3.6 is a schematic of the dispersed fluorescence experimental chamber.

A schematic of the dispersed fluorescence experiment is shown in figure 3.7. There is a differential pumping chamber between the beamline and the fluorescence that allows us to maintain a pressure differential of $10^{-6}$ Torr. This allows for a pressure of $10^{-3}$ Torr in the fluorescence chamber and $10^{-9}$ Torr of the sample gas at the end of the beamline. The gas was introduced normal to the incident radiation with an unskimmed supersonic molecular beam or an effusive jet. Below the interaction region is a mirror, and above it is a lens that collimates the fluorescence onto a plane mirror in the “optic box,” a light-tight box used for steering and focusing the fluorescent radiation on the entrance slit of the fluorescence monochromator. These studies used two monochromators, a THR 1000 and SPEC 500M. The gratings used had 3600
grooves/mm. The emission monochromator is operated at a resolution of 1 nm for the THR 1000 and 2.8 nm for the SPEC 500M. Fluorescence photons are then collected with optical multichannel analyzer (Princeton Instruments #LN/CCD-1024-EUV***).

3.8 Data Analysis

The data analysis for these experiments is straightforward, and only a few points require discussion here. Analysis of the dispersed fluorescence experiments has been discussed in detail elsewhere.\textsuperscript{53,55,56} For the photoelectron experiments, the procedures were straightforward. First, the photoelectron spectra must be corrected for the kinetic energy dependent transmission function of the analyzer, which is determined by using known photoelectron spectra. Then, the vibrational branching ratios are determined by finding the areas under the peaks, and taking ratios (typically with the ground vibrational level being the denominator). For peaks that are well isolated from other peaks, the area is determined by integration using existing software that was written in the lab.\textsuperscript{34} However, there are a few peaks that are quite close to one another, for example the 100 and the 020 vibrational modes in CO$_2$ and CS$_2$. A canned software package was used to fit each peak in a spectrum with a Gaussian function. Great care was taken to make sure all the Gaussians within a spectrum had the same width. This allowed for very high quality fits of the data, and very reliable branching ratios.
CHAPTER FOUR : CO $4\sigma^{-1}$ PHOTOIONIZATION

One of the many useful aspects of photoionization is that it provides information and insights on anisotropic scattering dynamics. $^{32,65}$ An electron leaving a molecular system senses the microscopic details of the potential, and the way that the photoelectron motion and the nuclear vibrational motion can become intertwined will depend on those details. Such studies help illuminate some primary aspects of chemical physics, i.e., how electronic and nuclear degrees of freedom are correlated. In doing such studies, surprising results can be obtained. Previous studies have focused on rotationally resolved aspects of valence isoelectronic systems $^{7,65,74}$, and markedly different behavior was observed. In this chapter there is a comparison for the vibrationally resolved photoionization behavior of two valence isoelectronic processes, CO $4\sigma^{-1}$ photoionization and N$_2$ $2\sigma_u^{-1}$ photoionization. They exhibit remarkably different behavior from each other, as we will see. For the case of the N$_2$ $2\sigma^{-1}$ photoionization there is a Cooper Minimum causing non-Franck-Condon behavior over 100 eV past the ionization energy $^{32}$, and this has been studied previously. However, the isoelectronic CO $4\sigma^{-1}$ photoionization has a shape resonance close to the ionization energy responsible for low energy deviations from Franck-Condon behavior. However, the high energy behavior of the CO $4\sigma^{-1}$ vibrational branching ratios has not been published previously, and the work reported here completes this picture and serves to introduce the bulk of the research which is presented on polyatomic systems in later chapters.

The vibrational branching ratios are determined for the CO$^+$(B$^2\Sigma^+$) state by measuring the dispersed fluorescence from the excited state ion. This study covers the spectral range from the ionization threshold to $h\nu_{exc}=185$ eV. The measurement of the
vibrational branching ratios over a broad range allows for a “global” perspective of photoionization. A major result that emerges from this is that the valence isoelectronic systems of CO and N$_2$ have qualitatively different behavior in their scattering dynamics far from the ionization threshold. This is of considerable interest because the normal assumption is that molecular effects are only significant in the region near the ionization threshold. This study also emphasizes a theme, namely, that detailed understanding of the scattering dynamics surface clearly when the molecular aspects (i.e., vibrational, rotational, alignment) are probed directly. In the case of CO$^+(B^2\Sigma^+)$, vibrationally resolved measurements are used to highlight the distinctions between valence isoelectronic diatomic systems.

4.1 Background on N$_2$ 2σ$_u^{-1}$ and CO 4σ$^{-1}$ Photoionization

The N$_2$ and CO photoionization have been the focus of several investigations. The first relevant study was done by Dehmer and Dill, not for the valence ionization of these molecules, but rather on calculations on the K-shell photoionization spectrum for N$_2$ and CO. Davenport calculated photoionization cross sections for CO from 20 to 40 eV. The calculations predicted a shape resonance in the CO$^+(B^2\Sigma^+)$ state, and this was confirmed by Plummer et al. measuring the experimental branching ratios and cross sections for N$_2$ and CO over the energy range 14 to 50 eV. Samson and Gardner also measured partial photoionization cross-sections and branching ratios for the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$ states for CO over the kinetic energy range of 1.4 to 4.6 eV. Gardner and Samson measured the vibrational intensity distribution from photoionization for N$_2$ and CO over the energy range of 1.4 to 4.6 eV, albeit with nontunable resonance lamp excitation sources.
There have been studies of the broad range rotational distributions for these two systems. Poliakoff et al.\textsuperscript{74} measured the rotational distributions for N\textsubscript{2} from 0 \leq E\textsubscript{k} \leq 200 eV and for CO from 0 \leq E\textsubscript{k} \leq 125 eV. The rotational study observed an intense $l = 3$ shape resonance in the CO $4\sigma \rightarrow k\sigma$ continuum. This was also confirmed via symmetry labeling polarization studies by Das et al.\textsuperscript{65} Vibrational distributions were measured in another study by Rao et al.\textsuperscript{32}, and deviations from Franck-Condon predictions were observed over a broad range. The presence of Cooper minima in the N\textsubscript{2} $2\sigma\text{u} \rightarrow k\sigma\text{g}$ continuum was the cause for the non-Franck-Condon behavior. Specifically, theoretical work demonstrated that the $l = 4$ and $l = 2$ partial waves had pronounced dips assigned to Cooper minima. Another rotationally-resolved study by Farquar et al.\textsuperscript{7} studied the rotational substructure for both the $v^+ = 1$ and $v^+ = 0$ levels of CO$^+$ ($B^2\Sigma^+$), and an improved liquid nitrogen cooled nozzle was used in this work. Much lower rotational temperatures resulted from the cooled nozzle, and the populations in the lower rotational levels were enhanced. The data in this was of higher quality then the previous studies\textsuperscript{65,74} resulting from the increased quantum efficiency of the CCD detector and the lower target rotational temperature. In the study by Farquar, calculations using Schwinger variational method was also presented, and the results of these calculations are pertinent for the work presented in this chapter.

The calculations and experiments demonstrated some surprising results. There were weak Cooper minima observed in a couple of the partial waves, and this was reflected in two ways. First, the rotational distributions exhibited weak, but observable deviations in the photon energy range from 30-100 eV. Secondly, the rotational distributions for the $v^+ = 0$ and 1 levels of the ion showed slight differences from each
other in this same energy range. So the current study is an attempt to see how the vibrational branching ratios for CO $4\sigma^{-1}$ ionization compare to those for $N_2$ $2\sigma_u^{-1}$ photoionization over a comparable energy range.

### 4.2 CO $4\sigma^{-1}$ Photoionization Results

In figure 4.1 the vibrationally resolved fluorescence spectrum of CO$^+(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ is measured at an excitation energy $h\nu_{exc} = 35$ eV. The features to note are the fluorescence transitions originating from $v^+ = 0, 1, and 2$ levels of the CO$^+(B^2\Sigma^+)$ state. The spectroscopic assignments are based on previous work. The intensity ratios are used to generate the vibrational branching ratios. The spectrum is measured using incident photon energy from 20 to 185 eV. The intensity ratios are a relative measure of the vibrational branching ratio but not the absolute values (as discussed in Chapter 3). The intensity ratio is proportional to the values of interest, the vibrational branching ratios. The relationship between the intensity ratios and the vibrational branching ratio is given by

\[
\frac{\sigma_{v_1 v_1}}{\sigma_{v_2 v_2}} = \frac{I_{v_1 v_1}}{I_{v_2 v_2}} \cdot \frac{q_{v_1 v_1}}{q_{v_2 v_2}} \cdot \left( \frac{\nu_{v_1 v_1}}{\nu_{v_2 v_2}} \right)^3 \cdot \frac{\Phi_{v_1}}{\Phi_{v_2}} \tag{4.1}
\]

Here $I_{v^+ v^+}, q_{v^+ v^+}, \nu_{v^+ v^+}, \Phi_{v^+}$ denote the intensity, the Franck Condon Factor, the transition frequency, and the fluorescence quantum yield, respectively. In a prior study, the intensity ratios $\frac{I_{v_1 v_1}}{I_{v_2 v_2}}$ were normalized to the vibrational branching ratios $\frac{\sigma_{v_1 v_1}}{\sigma_{v_2 v_2}}$ determined from photoelectron spectroscopy, and the current results are treated in this way too. The key point, though, is that it is the shape of the vibrational branching ratio curve that is most important, not the scale of the branching ratio data.
Figure 4.1 The vibrationally resolved fluorescence spectrum of CO\(^+(B^2\Sigma^+ \rightarrow X^2\Sigma^+)\), measured at \(h\nu_{\text{exc}} = 35\) eV.

Figure 4.2 shows the vibrational branching ratios in the low energy range (20 to 60 eV). The data shows that the ratios of two alternative vibrational levels as a function of photon energy are not constant. This non-FC behavior is in the region of the \(4\sigma \rightarrow k\sigma\) shape resonance in the \(l = 3\) partial wave.\(^{7,65,74}\) The measurements are consistent with previous studies,\(^{7,65,74}\) although the previous studies only focused on the shape resonant
region. The $v^+/v^+ = 1/0$ ratio will be extended to higher energy and compared to $N_2^+ 2\sigma_u^{-1}$ ionization. The $v^+/v^+ = 2/0$ is difficult to extend to higher energy with any precision due to scatter in the data at higher energy. (This is because the cross section decreases with increasing photon energy and the $v^+ = 2$ level is very weak, at best.) It should also be noted that fluorescence from the $v^+=3$ level was detected. However, the signal was too weak to obtain reproducible data.

Figure 4.2 The vibrational branching ratios for CO $4\sigma^{-1}$ photoionization in the low energy range (20 to 60eV). The non-FC behavior is due to the $4\sigma \rightarrow k\sigma$ shape resonance.
The data in figure 4.2 for the $v^+/v^+=0$ ratio is extended to much higher energy and shown in Figure 4.3. This figure shows an interesting result of the current study: the comparison of the CO$^+$ $4\sigma^{-1}$ and the N$_2$ $^2\sigma_u^{-1}$ photoionization from a previous work. 78

There are theoretical 7,32,65,74,78 and experimental data sets for both the CO$^+$ $4\sigma^{-1}$ and the N$_2$ $^2\sigma_u^{-1}$ photoionization. The agreement between the experiment and theory is excellent. The CO data show a strong deviation from Franck-Condon behavior at lower energies (closer to threshold) because of the $4\sigma \rightarrow k\sigma$ shape resonance mentioned above. N$_2$ has Cooper minimum that lead to non-Franck-Condon behavior far past threshold. 32 It is clear from the data that the two systems are qualitatively different. The implications of these results will be discussed in the following section.

![Figure 4.3 Vibration branching ratios, N$_2$ $^2\sigma_u^{-1}$ photoionization compared to CO$^+$ $4\sigma^{-1}$ ionization over an extended energy range](image)

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We will attempt to understand the meaning of the data contained in Figs. 4.2 and 4.3. Let’s concentrate first on Fig. 4.3, which shows the comparison between the N₂ and CO results. The electron configuration of CO-\{ \text{K,K, } (3\sigma)^2, (4\sigma)^2, (1\pi)^4, (5\sigma)^2 \} and N₂ is -\{ KK (2\sigma_g)^2, (2\sigma_u)^2, (1\pi_u)^4, (3\sigma_g)^2 \}. The labeling difference comes from the fact that N₂ has a center of inversion symmetry; this has implications for the photoelectron behavior, as we will see. The CO 4\sigma^{-1} case exhibits strong deviation from Franck-Condon in the lower energy region \(h\nu < 50\ eV\). It is well known that there is a shape resonance in the 4\sigma \rightarrow k\sigma channel.\[^7,65,74\] In Fig 4.3, the data cover a much wider range, and the data show not only the effect of the \(l = 3\) resonance at lower energies, but the qualitative differences over the whole range studied. Recall that this feature resonates in the \(l = 3\) partial wave, but this partial wave cannot exist in N₂, because excitation from an ungerade orbital (such as the 2\sigma_u) can only produce even partial waves.

The higher energy region, i.e., \(h\nu > 50\ eV\), is essentially featureless for CO while the more pronounced Cooper minima in N₂ lead to clear deviations from Franck-Condon behavior for \(h\nu \geq 100\ eV\). While the weak Cooper minima did show up in the rotationally resolved work of Farquar \textit{et al.}\[^7\], they did not influence the vibrational branching ratios for CO.

This study determined the vibrational branching ratios for \(CO^+(B^2\Sigma^+ \rightarrow X^2\Sigma^+)\) transition in the range \(20 \leq h\nu_{\text{exc}} \leq 185\ eV\). At low energies, there are strong deviations from Franck-Condon behavior, and this is in good agreement with previous measurements that showed the existence of a shape resonance in the 4\sigma \rightarrow k\sigma channel.
Cooper minima in N₂ lead to large deviations from Franck-Condon behavior, while the Cooper minima in CO are much less pronounced and the effect on the broad range behavior is minimal. Currently it is unclear why there is a discrepancy between the two molecules.

The primary focus of this discussion has been on the valence shell work. As mentioned previously, some of the first studies by the Dehmer and Dill focused on K-shell photoionization. The K-shell photoionization in CO has been extensively studied. Shigemasa et al. measured the C K-shell spectrum of CO molecules in the region of the \( \sigma^* \) resonance. Their results show that mixing of the \( d \) and \( f \) partial waves in the \( \sigma^* \) shape resonance occurs. It is not clear if such mixing effects also occur for the valence state studied here, but that is an issue worth investigating theoretically, and such studies are now underway. Before moving on to the polyatomic systems, it is worthwhile highlighting some of the main lessons obtained from this diatomic work. First, vibrationally resolved studies are very powerful probes into the molecular photoionization process, and some surprising results can emerge from such studies. Secondly, it is desirable to compare chemically related systems, and the CO/N₂ comparison presented above will be generalized to allow for comparisons between similar triatomic systems in later chapters. Finally, an implicit lesson is that it will be desirable to study as many related systems as is possible and practical, and this means leaving behind the dispersed fluorescence method employed in this chapter (and by other students in my research group), and using some of the more flexible and modern methods made possible using high resolution photoelectron spectroscopy at third generation synchrotron radiation sources.
CHAPTER FIVE : \( \text{CO}_2 \, 4\sigma_g^{-1} \) PHOTOIONIZATION

5.1 Introduction

As discussed previously, the case of \( \text{CO}_2 \, 4\sigma_g^{-1} \) photoionization was ideal for studying mode-specific behavior over a broad range. First, it is well known that nominally forbidden vibrational transitions occur for this case.\(^{15,17,87-89}\) Secondly, there is a well-documented continuum shape resonance.\(^{90-92}\) Thirdly, the shape resonance is relatively isolated, so any analysis focusing on its effects is expected to be straightforward. On a more general note, this broad range study allows one to elucidate the correlation between nuclear and electronic degrees of freedom. In this investigation, it was possible to probe all of the vibrational degrees of freedom, symmetric stretch, bending, and asymmetric stretching. This allows for a “global” view of photoionization and how a continuum electron can couple to alternative vibrational modes in a polyatomic molecule. It is the first such study of this type.

5.2 Background on \( \text{CO}_2 \, 4\sigma_g^{-1} \) Photoionization

The case of \( \text{CO}_2 \, 4\sigma_g^{-1} \) photoionization has attracted a large amount of interest historically. As a result, much of the background work necessary for the analysis of my data has been done. An overview of the most relevant studies will now be presented.

First, HeI resonance lamp (hv =21.2 eV) photoelectron spectra\(^{93}\) and threshold photoelectron spectra\(^{19}\) have been generated, so the assignments of all of the principal electronic bands – as well as the vibrational substructure for most of these electronic states – have been ascertained with high precision. In particular, the literature contains several studies employing photoelectron spectroscopy with relatively high resolution, i.e., \textit{ca.} 10 meV. This is significant, as these studies demonstrate that this resolution is
sufficient to separate all of the principal features in the CO$_2^+$ ($C^2\Sigma_g^+$) photoelectron spectrum. Thus, these studies not only identify the vibrational structure and assignments for the CO$_2^+$ ($C^2\Sigma_g^+$) state, they also provide an indication of the resolution that will be required for studying energy dependence of the vibrational structure.

In addition to the photoelectron spectroscopy experiments at a fixed energy, there has also been significant energy-dependent work, albeit without the benefit of vibrational resolution. These energy-dependent photoionization studies have uncovered autoionization and shape resonance structure.\textsuperscript{33,90} The $4\sigma_g \rightarrow k\sigma_u$ shape resonance has been the main focus of much of the experimental work.\textsuperscript{90-92} The first measurement of the $4\sigma_g \rightarrow k\sigma_u$ shape resonance was done by Carlson et al.\textsuperscript{91,92} They measured the energy dependence of the photoelectron asymmetry parameter ($\beta$) for the CO$_2$ $4\sigma_g^{-1}$ photoionization over the energy range $20 \leq h\nu \leq 65$ eV. This was vibrationally unresolved work. A pronounced dip in the asymmetry parameter was observed at $h\nu_{exc} \approx 42$ eV. This resonance dip was assigned to the $4\sigma_g \rightarrow k\sigma_u$ shape resonance. The partial photoionization cross-sections for the CO$_2$ $4\sigma_g^{-1}$ photoionization were first measured by Carlson et al.\textsuperscript{90-92} Brion and Tan\textsuperscript{94} used results on low-angle inelastic (e-2e) scattering, and observed a broad maximum in the optical strength that is most likely cause by this shape resonance. Siggel et al.\textsuperscript{90} measured the partial cross sections and asymmetry parameters for the $X^2\Pi$, $A^2\Pi$, $B^2\Sigma^+$ and $C^2\Sigma^+$ states from $20 \leq h\nu \leq 50$ eV. This study observed another minimum in the asymmetry parameter at $h\nu_{exc} \approx 22$ eV that they concluded was continuum-continuum coupling between the $B^2\Sigma^+$ and $C^2\Sigma^+$ states. The experimental partial photoionization cross sections for the $4\sigma_g^{-1}$ photoionization show a
large peak at $h\nu \approx 38$ eV. There is evidence that the trapping is of the $h$-wave ($l = 5$) component of the $\sigma_u$ continuum wave function by a shape resonance barrier. This is the largest angular momentum shape resonance observed in a molecular photoionization spectrum. Another important experiment was discussed in Chapter 2 and will be reviewed again. The work of Roy et al. studied $\beta$ for the (000) and (101) levels over the range 20-29 eV. They found the energy dependences for the (000) and (101) $\beta$ parameters were different. They hypothesized that Herzberg-Teller vibronic coupling was the mechanism responsible for populating the (101) level. The vibronic symmetry for the $C^2\Sigma_g^+, \nu^+ = (101)$ level can be calculated by taking the direct product of the electronic and vibrational wavefunctions, i.e., $\Sigma_g \otimes \Sigma_u = \Sigma_u$. Thus, they argue that the state from which the intensity was being “stolen” was the $B^2\Sigma_u^+$ electronic state. As a result, one would expect that the $\beta$ parameter for the CO$_2^+$($C^2\Sigma_g^+$), $\nu^+ = (101)$ level should track that of the $B^2\Sigma_u^+$ state. This is in fact what they found and they concluded that Herzberg-Teller interchannel coupling was the operative mechanism. We have utilized a similar method for determining the mechanism responsible for inducing the nominally forbidden transition that is similar. Specifically, we generate vibrational branching ratios from photoelectron spectra and use an analogous symmetry analysis.

The assignment of the level designated as (101) has been the topic of considerable debate. The assignment has been discussed in detail by Baer and Guyon, who suggest the (101) assignment. Eland and Berkowitz favor a (011) designation and Grimm and Larson present arguments in favor of $\nu^+ = (001)$. We support the $\nu^+ = (001)$ assignment, and that will be discussed shortly. However, it is fortunate that it will not matter a great deal whether the assignment is (101) or (001). To see this, recall that in the study of
Roy et al.\textsuperscript{18}, the Herzberg-Teller analysis relied on knowing the total symmetry of this level. They used the assignment (101). The Herzberg-Teller arguments are the same for either the (101) or the (001), so the assignment will not influence the analysis in any case. In the subsequent discussion, I will refer to this peak as the (001) vibrational level.

There have been many theoretical calculations that have examined the position and the width of the experimental values for the $4\sigma_g \rightarrow k\sigma_u$ shape resonance. The first calculations of this resonance were done by Swanson\textsuperscript{96} and Grimm\textsuperscript{97,98} using the multiple scattering method. The initial results of the two groups were in good agreement. The multiple scattering results predicted the position of the resonance to be lower than 42 eV with a narrower width than the experimental results. There was a great deal of theoretical effort, and there was considerable debate on the significance of the width of this feature.\textsuperscript{8,99-103,96,97,98,104} Most recently, state-of-the-art-Schwinger variational single channel calculations\textsuperscript{104} and multiple channel calculations\textsuperscript{104} were done by Lucchese. The single channel calculations produces a dip in $\beta$ that was too deep and again too narrow relative to the experimental data. The multiple channel calculation was successful in producing the correct magnitude and width of the experimental feature.

One of the main results that will follow is that symmetry forbidden vibronic features arise in the photoelectron spectrum. In order to develop a clear picture of how this occurs, we used our experiments to spur new theoretical work by Lucchese. These experiments and his theoretical efforts helped clarify the origin of the forbidden transitions and the energy dependence for their intensities. It has been shown that nominally forbidden transitions can become allowed as a result of instantaneous symmetry breaking.\textsuperscript{5,6,105} Herzberg suggests the possibility of such an intrachannel
mechanism (although he gives no examples), when inclusion of the vibrational part of the molecular wavefunction in the dipole matrix elements leads to non-zero dipole matrix elements. The dipole matrix elements are calculated as described in Chapter 2. If the Franck-Condon approximation is not invoked in equation 2.20 (i.e., if the electronic transition dipole moment is not factored from the vibrational integral), then it becomes possible for single quanta excitation of nontotally symmetric vibrations to occur because of the variation of the electronic matrix elements with changes in molecular geometry. The dipole matrix elements leading to the forbidden transitions can be enhanced in the presence of a continuum scattering resonance, leading to resonance-enhancement of forbidden transitions. To test these ideas, numerical calculations are presented which are based on the Schwinger variational method. The calculation was performed using single-channel frozen-core Hartree-Fock approximation (SCFCHF) by my collaborator, Prof. Robert Lucchese of Texas A&M University. Both the experimental and the theoretical results will be discussed in the next section.

5.3 Results of the CO$_2$ 4σ$^-1$ Photoionization

5.3.1 Photoelectron Spectra

Figure 5.1 shows the outer valence-shell photoelectron spectrum of CO$_2$. The outer valence configuration of CO$_2$ is …(4σ$^g$)$^2$(3σ$^u$)$^2$(1π$^u$)$^4$(1π$^g$)$^4$, and ionization energy of each orbital is 19.394 eV, 18.077 eV, 17.315 eV, and 13.778 eV, respectively. Our results for the IP’s were consistent with previous measurements that were limited to resonance lamp excitation.
Figure 5.1 The outer valence-shell photoelectron spectrum of CO$_2$.

Figure 5.2 shows the portion of the photoelectron spectrum containing the CO$_2^+$($C^2\Sigma_u^+$) state, and this spectrum was acquired at an excitation energy of $h\nu= 42$ eV, which corresponds to a resonant excitation condition, as will be shown later. On inspection of the spectrum, we see five moderately-intense and well-resolved features, the ground state ($v^+ = 000, E_b=19.3944$ eV), excitation of the bending mode ($v^+ =010, E_b=19.4705$ eV), two quanta excitation of the bend ($v^+ =020, E_b=19.5432$ eV), the symmetric stretching mode ($v^+ =100, E_b=19.5460$ eV), and the asymmetric stretching mode ($v^+ =001, E_b=19.7568$ eV). There are also two weaker features that “light up” at this excitation energy. These weaker features occur at binding energies of 19.620(5) eV
and 19.642(5) eV, and they are assigned as excitation to the $v^+ = (030)$ and $(110)$ levels, respectively.

![CO$_2$ C$^1\Sigma_g^+$ photoelectron spectrum - on resonance](image)

Figure 5.2 The photoelectron spectrum showing the CO$_2^+$ ($C^2\Sigma_g^+$) state. This spectrum was acquired at the resonance excitation energy of $h\nu_{exc} = 42$ eV.

Working at high resolution, the results were extremely sensitive to Doppler broadening as the photoelectron kinetic energy increased. The origin of Doppler broadening was discussed in section 3.6. The broadening can be calculated with
equation 3.6. Consider that the $v^+ = (020)$ is only separated from the $v^+ = (100)$ by 23 meV. For CO$_2$ at 293 K, an electron with 10 eV of kinetic energy will have Doppler broadening of 8.5 meV; for an electron with $E_k = 100$ eV, the broadening is 27.0 meV. Therefore at high electron kinetic energies these two peaks are no longer resolved. If the initial temperature of CO$_2$ was 15 K (a readily achievable temperature in a supersonic molecular beam expansion), the broadening would be reduced to 1.8 meV for 10 eV photoelectron and 6.1 meV for a 100 eV photoelectron.

The loss of resolution due to Doppler broadening complicated the data analysis somewhat. Direct integration of the peaks was not possible, so the (020), (100) and (030), (110) vibrational modes were fitted with Gaussian functions using commercially available peak fitting software. The relative area of the 020 was assumed to be constant and the area of the 100 was adjusted to generate the 100/000 vibrational branching ratio. The assumption that the 020 relative intensity was constant with energy was borne out by the fits of the data, and making this assumption resulted in much less scatter for the 100/000 branching ratios. Knowing the energy separation of the two peaks, the center of the Gaussians could be placed at the center of the peaks. The widths within a given spectrum were held constant. The fitted area under the peaks was used to calculate the vibrational branching ratios.

5.3.2 Vibrational Branching Ratio Curves

In trying to uncover the mechanism responsible for the appearance of the forbidden transitions in the CO$_2$ $4\sigma_g^{-1}$ photoionization, vibrational branching ratios are measured over a broad range, $20 \leq h\nu \leq 110$ eV. Broad spectral coverage allows for interrogating the slowly varying aspects of photoionization. The branching ratio is
calculated by the integrating the area under the peaks (by fitting in cases where necessary, as discussed above).

The $\text{CO}_2 4\sigma_g^{-1}$ photoionization vibrational branching ratios are shown in figure 5.3. The experimental vibrational branching ratios for the (010)/(000), (100)/(000) and the (001)/(000) branching ratios are shown in the left-hand frames over the energy range $20 \leq h\nu \leq 110$ eV. On the right-hand side are the (110)/(000), (020)/(000), and (030)/(000) vibrational branching ratios over the range $20 \leq h\nu \leq 70$ eV. The (110)/(000) and (030)/000 also have maxima at $h\nu \approx 42$ eV. The (020)/(000) exhibits little energy dependence and is essentially featureless over the range studied. The excursions in the vibrational branching ratio curves at $h\nu = 42$ eV clearly result from the $4\sigma_g \rightarrow k\sigma_u$ shape resonance. It should also be noted the intensities of the (010)/(000) and (001)/(000) vibrational branching ratios (relative to that of the 100/000) is surprising. The point is that magnitude of the branching ratios for the forbidden vibrations is comparable to those of allowed excited vibrations.

5.4 Discussion of CO$_2$ 4\sigma_g^{-1} Photoionization

5.4.1 Bending Mode and Asymmetric Stretching Modes (Experimental)

The photoionization dynamics for CO$_2$ 4\sigma_g^{-1} photoionization has been studied in detail by the Carlson et al. $^{91,108}$ and Siggel et al. $^{90}$ as discussed previously. Both groups observed a pronounced dip at $h\nu = 42$ eV in the photoelectron asymmetry parameter. This dip was assigned as the $4\sigma_g \rightarrow k\sigma_u$ shape resonance. Figure 5.4 shows the vibrational branching ratio for the bending vibration (010/000) in the bottom frame and the energy dependence of the photoelectron asymmetry parameter curves $^{90,108}$ in the top frame. The vibrational branching ratio is going through a maximum at the same energy

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that $\beta$ is going through a minimum. The fact that the $(010)/(000)$ vibrational branching ratio curve the photoelectron asymmetry parameter curve\textsuperscript{90,108} have their excursions at the same energy is the first piece of evidence that the $4\sigma_g \rightarrow k\sigma_u$ shape resonance plays some role in the excitation of the forbidden bending vibration.

Figure 5.3 The $\text{CO}_2^+(C^2\Sigma_g^+)$ state vibrational branching ratios.
Photoelectron spectra encompassing all of the valence electronic states of CO$_2$ (such as those shown in figure 5.1) were obtained over the range $20 \leq h\nu \leq 100$ eV and used to calculate electronic branching ratios to compare the vibrational branching ratios. This was done to evaluate whether interchannel coupling was responsible for the forbidden vibrational levels. This is a direct analogy to the analysis performed by Roy et al. $^{18}$ If the 010 level is gaining intensity via interchannel coupling, one must evaluate the total vibronic symmetry of the CO$_2$(C$^2\Sigma^+_g$, $\nu^+=010$) level. The electronic symmetry is $\Sigma_g$ and the vibrational symmetry is $\Pi_u$, so the total vibronic symmetry is given by the direct product, $\Sigma_g \otimes \Pi_u = \Pi_u$. The only nearby $\Pi_u$ state is the $A^2\Pi_u$ state, so the intensity of the CO$_2$(C$^2\Sigma^+_g$, $\nu^+=010$) level should track that of the $A^2\Pi_u$ state, and the (010)/(000) vibrational branching ratio should track that of the $A^2\Pi_u/C^2\Sigma^+_g$ electronic branching ratio. These comparisons are shown in figure 5.6 and is clear from the data that the (010)/(000) and the $A^2\Pi_u/C^2\Sigma^+_g$ electronic branching ratio do not track one another. On the other hand, the interchannel coupling argument applied to the 001 level suggests that this level’s total vibronic symmetry is $\Sigma_g \otimes \Sigma_u = \Sigma_u$, so it is expected that the intensity would be originating from the nearby $B^2\Sigma^+_u$ state. Indeed, the (001)/(000) vibrational branching ratio curve and $B^2\Sigma^+_u/C^2\Sigma^+_g$ electronic branching curve track each other closely, corroborating the analysis of Roy et al. $^{18}$, and demonstrating that the Herzberg-Teller mechanism is consistent with the observed energy dependence.
Figure 5.4 The bottom frame shows the new results, the energy dependence of the vibrational branching ratio for the forbidden bending excitation. The top frame shows the energy dependence of the photoelectron asymmetry parameter from the investigation of Carlson et al. and Siggel et al. The vibrational branching ratio is going through a maximum at the same energy $\beta$ is going through a minimum. The implication is the shape resonance is responsible for the intensity in bending vibrational branching ratio.
Figure 5.5 Herzberg-Teller analysis for the forbidden 001 and 010 modes, if Herzberg-Teller coupling was the mechanism for the intensity in the forbidden modes the (010)/(000) should track the $A^2\Pi_u/C^2\Sigma_g^+$. No clear agreement is observed with the two curves. However, there is good agreement with the (001)/(000) and the $B^2\Sigma_u^+ / C^2\Sigma_g^+$ supporting the Herzberg-Teller mechanism.

5.4.2 Comparison of Vibrational Branching Ratios with Schwinger Variational Calculations (Single-Channel Analysis)

As mentioned previously, theoretical work was done by Prof. Robert Lucchese, and his efforts involved calculating the continuum electron wavefunction, as well as the
associated dipole matrix elements that determine the partial photoionization cross section. There are two points deserving of particular emphasis regarding his calculations. First, they did not incorporate non-Born-Oppenheimer contributions that are responsible for Herzberg-Teller coupling, as they were carried out using Hartree-Fock level wavefunctions (including that of the continuum electron) and they used an adiabatic treatment of the vibrational motion (i.e., strictly Born-Oppenheimer). Secondly, the calculations did not invoke the Franck-Condon approximation. The results are shown below in Fig. 5.6

There are several insights revealed from the comparison between the experimental and theoretical results. The shapes of the theoretical curves and experimental curves agree very well for the (010)/(000) and (001)/(000) curves, but not for the (100)/(000) curve. Let’s first consider the (010)/(000) results. The previous discussion indicated that the interchannel coupling mechanism was not consistent with the observed energy dependence for the bending excitation. This comparison with theory based on an intrachannel coupling mechanism demonstrates excellent agreement. The conclusion that we draw from this is that intrachannel coupling induced by the continuum electron is the underlying cause for the excitation of this nominally forbidden transition. Because this forbidden transition is so strongly influenced by the continuum shape resonance, I refer to this phenomenon as resonantly-amplified vibronic symmetry breaking. Also, because this effect would not arise unless the electronic part of the matrix element shows strong variation with the bending vibration, these results imply that this shape resonance is strongly dependent on bond angle. This is an important new result, as most previous work on molecular shape resonances suggest that they are sensitive to bond lengths, but
have neglected their sensitivity to alternative types of geometric distortions, including bond angle and bond torsion motions.

Fig. 5.6 Comparison of the experimental and single-channel adiabatic calculations for the CO$_2$ ($C^2\Sigma_g^+$) vibrational branching ratios. Calculations were performed only for the (010)/(000), (100)/(000) and the (001)/(000) over the energy range $20 \leq h\nu \leq 110$ eV. The agreement with theory and experiment is good except for the (100)/(000) ratio. The agreement for the asymmetric stretch adds some ambiguity for the interpretation, as discussed in the text.
The branching ratio for the symmetric stretch, (100)/(000), is quite interesting. The experiment displays a pronounced dip that occurs exactly at position of the shape resonance. Agreement with theory is poor, and we will return to this comparison in a moment. However, it is important to emphasize that a resonant dip has never been observed for a shape resonance, although so-called window resonances are common for electronic autoionization processes. The expectation is that one would see a peak, or perhaps an asymmetric peak, or no deviation at all. Shape resonances affect weaker channels more dramatically than strong channels, therefore the partial cross section for an excited vibration such as (100) level would is expected to have a greater relative increase in its cross section relative to transition populating the (000). The resulting branching ratio should have a maximum. It is not uncommon for peaks to be asymmetric with one wing having a dip, because shape resonance positions can shift with internuclear separation. There are unusual cases such as CS$_2$ and Cl$_2$, where the shape resonance has $k\pi$ symmetry, so the continuum wavefunction localization (i.e., enhancement) occurs away from the molecular axis. For these cases, the shape resonances show little sensitivity to the changes in the internuclear separation, i.e. bond length. In such cases, the branching ratio curves are featureless. However, even these unusual $\pi$ shape resonances do not explain the occurrence of a “window resonance,” i.e., the resonant dip observed in Fig.5.3. and Fig 5.6. Window resonances are common for multichannel phenomena, such as electronic autoionization processes. They were first described in the context of Fano’s seminal work on the interaction of a discrete level with an underlying continuum. They result from the destructive interference between discrete excitation and underlying continua. However, window
resonances corresponding to autoionization phenomena are not plausible explanation for the current observations in CO$_2$. Such resonances are very narrow typically $\Delta E < 0.1$ eV. The vibrational branching ratio resonance observed in the present study is approximately 10 eV wide. While the current result may well result from some type of destructive interference, it is not clear what the underlying mechanism is. The point is that the shape resonance is actually *suppressing* the production of the (100) level. This is worthy of additional study in its own right. There is the hint of a local minimum in the theory curve, and Lucchese has noted that this dip is very sensitive to the parameters (e.g., equilibrium bond length) used in the calculations. The point is that the calculation is not yet in final form, and better agreement may yet emerge. If so, the sensitivity of the branching ratio to the molecular parameters will be of particular interest in further interpretations of these data. If it turns out that agreement is not forthcoming, then additional theoretical efforts that investigate unanticipated interference effects (that might lead to destructive interference and hence cross-section suppression) will be needed. It should be mentioned that there is a small Fermi resonance coupling the (100) and (020) levels$^{19,113}$, and this might be a source of interference effects leading to destructive contributions to the (100) cross section.

Now let us turn our attention to the asymmetric stretch. The shape of the theoretical curve for the (001)/(000) agrees with experiment, but overestimates the magnitude of the branching ratio maximum by approximately a factor of four. This introduces considerable ambiguity into the interpretation that requires additional study. Previously, in the comparison shown in Fig. 5.5, we concluded that the vibrational branching ratio was consistent with the *interchannel* coupling mechanism. However, the comparison
between experiment and theory shown in Fig. 5.6 is consistent with the *intrachannel* coupling mechanism. One might argue that the disagreement between the magnitude of the effect between experiment and theory indicates that the other mechanism (interchannel coupling) is the culprit responsible for exciting the forbidden transition. However, there is no fixed scale appropriate for the interchannel mechanism. At this point, it appears that independent theoretical tests of the mechanism must be done, and they must not treat the y-axis of these comparisons as floating parameters.

### 5.4.3 Previously Unobserved Transitions

Finally, we turn our attention to some of the weaker features seen in Fig. 5.2, which was obtained at $h\nu = 42$ eV and illustrates a useful point. When the electron is ejected resonantly, weaker features frequently become more pronounced, and previously unobserved levels may become visible. Resonances are known to amplify weaker transitions, as explained for many of the previously studied diatomic systems. This is also the case in the present work on CO$_2$ at the photon energy of 42 eV, which shows two new vibrational features emerging. They are most intense at $h\nu \approx 42$ eV, the energy of the $4\sigma_g \rightarrow k\sigma_u$ continuum shape resonance. They are essentially unobservable except at the resonance energy. The new features are separated by 22 meV, and this energy separation is almost identical to the separation between the $v^+ = (020) \text{ and } v^+ = (100)$ peaks. They also appear 85 meV higher in binding energy then the $v^+ = (020) \text{ and } v^+ = (100)$. The energy spacing is almost exactly equal to the energy of the single quantum of $\nu_2$ vibration. Thus, it seems that the peaks are most probably due to $v^+ = (030) \text{ and } v^+ = (110)$ transitions. This underscores the point made above, namely, that resonant excitation can be used to “light up” modes that are normally unobserved. Work on radicals has used
This experimental strategy. \textsuperscript{114} This other work has focused on autoionization resonances, but shape resonances may also be used to observe weak transitions. The energy dependence of these vibrations is shown in figure 5.3. Both peaks rise from nearly zero background to a peak at $h\nu \approx 42$ eV, exactly as the $(010)/(000)$ had a maximum at $h\nu \approx 42$ eV. The branching ratios undergo drastic enhancement at the resonance energy, and their intensities are essentially zero off the resonance energy. This would explain why they have not been observed previously. However, it is curious that all of the peaks associated with bending show strong branching ratio excursion except for the $(020)/(000)$ curve. We do not understand this anomaly but it may be connected with the Fermi resonance between the $(100)$ and $(020)$ levels.

5.4.4 Summary of CO\textsubscript{2}\textsuperscript{+}(C\textsuperscript{2}\Sigma\textsubscript{g}+) Results

In summary, the agreement between theory and experiment is encouraging for the main feature – the excitation of one quantum of bending excitation – is excellent. We have assessed the origin of the nominally forbidden bending mode, and determined that it arises via an intrachannel effect related to the outgoing photoelectron. The intensity of the $(010)$ peak is unexpectedly strong. Vibrational branching ratios for allowed excited vibrational transitions are typically less than 10\% when the potential curves are similar for the neutral target and the ion; the forbidden bending excitation is comparable to this intensity at the resonance energy. Clearly, this demonstrates that this shape resonance is sensitive to the bond angle, and that this sensitivity is pronounced. The deviation from Franck-Condon behavior would not occur at all unless the trapping occurs differently for bent and linear geometries. \textsuperscript{5,6,35,106} Many studies have shown the sensitivity of shape resonances to breathing motions that alter the bond length, but this work and one
previous dispersed fluorescence study are the first to show that changes in bond angle can correlate with significant changes to the continuum electron wavefunction.

More generally, this study suggests that forbidden excitations are sometimes due to intrachannel effects, such as the photoelectron mediated mechanism elucidated here. Secondly, the data show that the vibrationally selected results are extremely sensitive to small changes in molecular geometry, including bond angle and bond length. Thirdly, the results demonstrate the utility of vibrationally resolved studies over a broad range for polyatomic molecules, as important processes which exert leverage on the photoionization scattering dynamics frequently are slowly varying.
CHAPTER SIX : \(5\sigma_u^{-1}\) PHOTOIONIZATION OF CS\(_2\)

The results of the CO\(_2\) \(4\sigma_g^{-1}\) photoionization are quite striking. It would be of great interest to see if the photoelectron mediated vibronic coupling mechanism is truly a general result. With this idea in mind, it is useful to study molecular systems of similar complexity. The \(5\sigma_u^{-1}\) photoionization of CS\(_2\) is an ideal candidate for a follow up study. It has the same molecular symmetry as CO\(_2\) and the isoelectronic \(3\sigma_u^{-1}\) channel in CO\(_2\) has demonstrated the photoelectron mediated vibronic coupling mechanism.\(^5,6,35,106\)

There are well known forbidden vibrational excitations observed in the \(5\sigma_u^{-1}\) photoionization of CS\(_2\).\(^{15,21,30,93}\) The photoelectron spectroscopy\(^{15,21,30,93}\) and dispersed fluorescence\(^{109,115}\) have been well-studied previously, but this new study broadens the range of kinetic energies accessed while at the same time investigating considerably more vibrational excitations. There is a well-documented continuum shape resonance at \(h\nu \approx 21\) eV,\(^{38,109}\) but the behavior at higher photon energies has never been investigated with vibrational resolution. As with CO\(_2\), we can study the symmetric stretch, asymmetric stretch, and bending vibrational degrees of freedom. The broad range study allows us to study the correlation between nuclear and electronic degrees of freedom. To foreshadow what will follow, CS\(_2\) will have a number of similarities with CO\(_2\), but important surprises and insights will emerge from the way in which the branching ratios contrast, as well.

6.1 Background on \(5\sigma_u^{-1}\) Photoionization of CS\(_2\)

As mentioned in the introduction to this chapter, \(5\sigma_u^{-1}\) photoionization of CS\(_2\) has been well studied. (The valence shell electronic configuration for CS\(_2\) is \((5\sigma_g)^2(4\sigma_u)^2\)
Both dispersed fluorescence and photoelectron spectroscopy have been employed experimentally in the past. The CS$_2^+$ ($B^2\Sigma_u^+ \rightarrow \chi^2\Pi_g$) dispersed fluorescence was studied by Balfour$^{115}$, while Kakar et al.$^{109}$ measured the partial photoionization cross sections for the $v^+ = (000)$ and (100) levels by measuring CS$_2^+$ ($B^2\Sigma_u^+ \rightarrow \chi^2\Pi_g$) dispersed fluorescence over the range $18 \leq h\nu_{exc} \leq 30$ eV. The results of Kakar$^{109}$ indicated that the branching (100)/(000) ratio was insensitive to the shape resonance feature at $h\nu = 21$ eV. Theoretical efforts to characterize that feature revealed that it a shape resonance with $\varepsilon\pi_g$ symmetry. Because it has $\pi_g$ symmetry, the quasi-bound electron has density away from the molecular axis$^{38,109}$ which is consistent with the lack of sensitivity of the shape resonance to the breathing vibration of the ion. One of the first highly resolved valence shell photoelectron spectra was measured by Brundle et al.$^{93}$ A supersonic gas jet was used by Wang et al.$^{15}$ to reduce the initial rotational temperature of the molecules, as well as reduce the Doppler width. Baltzer et al.$^{115}$ used a gas cell and a high resolution photoelectron analyzer following HeI (21.2 eV) fixed energy photoionization source, and they reported the highest resolution spectra. They also reported new vibrational features. The new vibrational features are the combination band ($v^+ = 120$, $E_b = 14.592$ eV), three quanta of bending ($v^+ = 030$, $E_b = 14.606$ eV), two quanta in the symmetric stretch ($v^+ = 200$, $E_b = 14.14705$ eV) combination band ($v^+ = 101$, $E_b = 14.713$ eV), combination band ($v^+ = 201$, $E_b = 14.788$ eV), two quantum of asymmetric stretch ($v^+ = 002$, $E_b = 14.002$ eV), combination band ($v^+ = 102$, $E_b = 14.876$ eV). All of these photoelectron studies used nontunable sources. There are also two synchrotron-based experiments that were performed that are relevant for the present study, one by Hikosaka and Mitsuke$^{30}$ and another by Carlson et al.$^{116,117}$ Hikosaka and
Mitsuke measured 2-dimensional photoelectron spectra from $14.60 \leq \hbar \nu \leq 15.35$ eV. This study clearly observed an autoionization resonance that preferentially populated the (001) bending mode at $\hbar \nu_{\text{exc}} \approx 14.88$ eV. My dispersed fluorescence measurements will focus on this energy range. With respect to my work over a broader spectral range using photoelectron measurements, the work of Carlson et al.\textsuperscript{116,117} is particularly relevant. Carlson et al.\textsuperscript{116,117} measured the partial photoionization cross-sections, angular distribution parameters, and also performed multiple scattering model calculations results for the first five electronic bands in CS$_2$ from $21 \leq \hbar \nu \leq 70$ eV. The experimental results in Carlson’s study were not vibrationally resolved, but they serve to identify potentially important continuum features. In this regard, the angular distribution parameters and multiple scattering calculations showed a pronounced dip at $\hbar \nu_{\text{exc}} \approx 46$ eV. Although this feature was not assigned (such as a shape resonance), they did conclude that it was not due to a Cooper minimum based on their multiple scattering calculational results. The vibrationally integrated cross section in this spectral range is relatively flat with a comparatively small value. However, we will see that vibrationally resolved photoelectron measurements serve to amplify continuum features of interest.

6.2 Results for 5$\sigma_u^{-1}$ Photoionization of CS$_2$

The 5$\sigma_u^{-1}$ photoionization of CS$_2$ was studied via dispersed fluorescence and photoelectron spectroscopy and the agreement between the data sets from the different methods is excellent, as will be seen below.

First, I will focus on the dispersed fluorescence results obtained at CAMD which include the lower energy region. A portion of the CS$_2^+$ ($B^2\Sigma_u^+ \rightarrow X^2\Pi_g$) fluorescence
The fluorescence spectrum has been studied extensively. The spectrum has two large well-defined peaks arising from fluorescence decay of the $v^+ = (000)$ level.

$$\text{CS}_2^+(B^2\Sigma_u^+ \rightarrow X^2\Pi_g)$$

![Fluorescence spectrum of CS$_2^+$](image)

Figure 6.1 A portion of the vibrationally resolved CS$_2^+$ ($B^2\Sigma_u^+ \rightarrow X^2\Pi_g$) spectrum. The incident photon energy was $h\nu = 15.7$ eV and the sample jet was cooled to 6 °C.
The doublet occurs because the ground state of CS$_2^+$ is a $X^2\Pi_g$ state and spin-orbit splitting produces two terminal levels for the fluorescence. The other vibrational feature of note is one originating from the $v^+ = (010)$ level. The fluorescence wavelengths are 2820 Å for fluorescence from the $v^+ = (000)$ level, and 2844 Å for fluorescence from the $v^+ = (010)$ level. The ratio of the fluorescence intensities is proportional to the vibrational branching ratio, as discussed in Chapter 2.

![Graph](image-url)

Figure 6.2 Temperature dependence of the $v^+ = (010)/v^+ = (000)$ intensity ratio in the CS$_2$ 5σ$_{u}^{-1}$ photoionization. There is a change in the magnitude of the branching ratios as the temperature is increased owing to the additional population of the $v^+ = (010)$ level resulting from hot-band ionization at the higher temperature.
Analysis of the dispersed fluorescence data can be complicated by hot band ionization, hence they should be strongly dependent on temperature. The spectra were taken at three different temperatures (228 K, 280 K, and 518 K) to ascertain the contributions from hot band ionization. The temperature dependent $\nu^+ = (010)/\nu^+ = (000)$ intensity branching ratios are in figure 6.2. It appears that the $\nu^+ = (010)$ in the CS$_2$ ($B^2\Sigma_u^+$) state is due to ionization of neutral molecules at a low temperature limit and there is no major contribution from hot band ionization at 280 K. Comparing the 228 K and the 280 K data sets, the two are almost identical. This comparison might be a little misleading, as one might conclude that there is no hot-band ionization occurring at these temperatures. A quick back-of-the-envelope calculation will indicate that such processes do contribute. The lesson from Fig. 6.2 is that the hot-band contribution is small (perhaps negligible) compared to creation of $\nu^+ = (010)$ from the ground vibrational level of the neutral molecule [i.e., $v_0=(000)$].

If hot band ionization was significant, the intensity in $\nu^+ = (010)$ would be reduced at the lower temperature and that would reduce the value of the intensity ratio. At 518 K, the $\nu^+ = (010)/\nu^+ = (000)$ intensity ratio clearly demonstrates how hot-band ionization can affect the results. At elevated temperatures the contributions from hot band ionization are now significant. The $\nu^+ = (010)$ level is increased at a greater rate because it can be produced via hot band ionization of the $v_0 = (000)$ level, so the relative intensity of fluorescence from the $\nu^+ +(010)$ level has increased. The interpretation of minimal hot-band “pollution” at lower temperatures will be reinforced by comparison of the fluorescence results with the photoelectron results (where hot band contributions are energy separated and identifiable as a result).
Figure 6.3 A portion of the vibrationally resolved photoelectron containing the CS$_2$($B^2\Sigma_u^+$) state at photon energies of 18 eV, 30 eV, 40 eV and 50 eV.

Let’s turn to the photoelectron results. The ALS beamline used in this study (10.0.1) was not able to access the region below 17 eV, so the autoionization feature was not
accessible. On the other hand, the high flux at higher energies allowed a more complete study of the continuum scattering dynamics, as we will see. Figure 6.3 shows a portion of the vibrationally resolved photoelectron containing the CS$_2^+(B^2Σ_u^+)$ state at photon energies of 18 eV, 30 eV, 40 eV and 50 eV. The spectra show six well-resolved features; the vibrational ground state ($v^+ = 000$, $E_b = 14.474$ eV), one quantum of bending ($v^+ = 010$, $E_b = 14.517$ eV) mode, one quantum of symmetric stretch ($v^+ = 100$, $E_b = 14.550$ eV), two quanta of bending ($v^+ = 020$, $E_b = 14.561$ eV), two quanta in the symmetric stretch ($v^+ = 200$, $E_b = 14.627$ eV), and one quantum of asymmetric stretch ($v^+ = 001$, $E_b = 14.637$ eV). The assignments agree with the published results.\textsuperscript{15,21,30}

There is a feature at higher binding energy than the (001) vibrational level labeled with a question mark in Fig. 6.3. This feature was not observed in previous studies\textsuperscript{15,21,30}, and no linear combination of vibrational frequencies matches the binding energy of this feature. At higher photon energies, the intensity of this feature drops essentially to zero. These observations suggest that this peak is most likely due to an impurity. There are also several other vibrational features for CS$_2$ assigned at higher binding energies that were not studied here\textsuperscript{21}. The (100) and (020) vibrational levels are separated by less than 10 meV, as are the (200) and (001) levels. To determine the peak areas associated with each of these levels, Gaussians are fitted to the vibrational peaks. The integrated areas are determined from the fits and are used to generate the vibrational branching ratios.

The dramatic dependence of the (010) and (001) levels on energy is apparent from a cursory inspection of figure 6.3. These levels gain considerable intensity in the spectrum acquired at $h\nu = 40$ eV, and these data provide a clear indication that something important is occurring in this energy range. These observations are consistent with the
vibrationally unresolved work of Carlson\textsuperscript{116,117}, where an excursion in the asymmetry parameter was observed in this region.

Figure 6.4 The vibrational branching ratios for CS\textsubscript{2} 5\sigma_u^{-1} photoionization over the energy range 18 \leq h\nu_{\text{exc}} \leq 80 \text{ eV}. For the 010/000 ratio, data were acquired using both dispersed fluorescence and photoelectron spectroscopy. The agreement between the fluorescence and photoelectron methods is excellent. Note that the (010)/(000) and (001)/(000) curves are quite similar with maxima at 42 eV.
To generate a clearer picture of how the relative vibrational intensities are changing, the energy dependence for all the vibrational modes in CS$_2$ were measured from $18 \leq h\nu \leq 80$ eV with photoelectron spectroscopy in an attempt to uncover the mechanism responsible for the enhancements of the forbidden vibrational excitations at 40 eV. Beamline 10.0.1 has a energy range of $17 \leq h\nu \leq 340$ eV $^{70}$, and the ionization threshold for the CS$_2$ ($B^2\Sigma_u^+$) state is 14.47 eV. Thus, the region near threshold was not accessible via the photoelectron studies, and it is well known that close to the ionization threshold, autoionization can greatly effect vibrational distributions. This is why the dispersed fluorescence presented earlier on the CAMD 3m TGM beamline were performed to complete this investigation.

The CS$_2$ 5$\sigma_u^{-1}$ photoionization was studied over the energy range $18 \leq h\nu_{\text{exc}} \leq 100$ eV, but are only reported up to 80 eV, since all of the ratios were flat beyond this energy. The allowed transitions are the (100), (020) and (002), and the forbidden vibrational modes are the (010) and (001). The allowed transitions are flat and featureless. The (010) and (001) forbidden transitions have large maxima at $h\nu_{\text{exc}} \approx 42$ eV. As we will see, the mode specificity alludes to the character of the continuum electron at 42 eV.

There are no calculations yet available to assign this apparent resonant behavior at this time, but we will see that the data provide experimental clues that provide hypotheses for theoretical and calculational studies to test.

6.3 Discussion of 5$\sigma_u^{-1}$ Photoionization Vibrational Branching Ratios

The only previous study of the CS$_2$ 5$\sigma_u^{-1}$ photoionization dynamics over a similar energy range as the current investigation was the vibrationally unresolved investigation
by Carlson et al. They measured the cross sections and the asymmetry parameter over the range $21 \leq h\nu_{exc} \leq 60$ eV, and also performed multiple scattering model calculations. The vibrationally unresolved asymmetry parameter curve showed a pronounced dip at $h\nu = 46$ eV. The feature was not assigned to anything specific such as a shape resonance or Cooper minima. Clearly, the feature reported by Carlson is the same feature that is trapping the electron in these studies.

Figure 6.5 The bottom frame shows the current 010/000 ratio curve, and the top frame shows the asymmetry parameter curve. The branching ratio is going through a maximum at approximately the same energy that $\beta$ is going through a minimum, suggesting that the same process is responsible for both excursions.
The study by Carlson indicated that this feature at 42 eV was not due to a Cooper minimum. Based on its width (ca. 10 eV) and position (ca. 20 eV above threshold), it is likely a shape resonance. Using this as a working hypothesis, it is possible to make some intelligent guesses as to the nature of how the quasibound electron is being localized for this state. It is tempting to guess that there is something related to symmetry-breaking that is the relevant issue, since the only two ratios showing appreciable deviations with energy are those corresponding to the forbidden vibrational modes: the (010) bending motion and the (001) asymmetric stretch. As discussed in the previous chapter, the symmetry of the modes are $\Pi_u$ and $\Sigma_u$ respectively. A similar Herzberg-Teller argument made for CO$_2$ can be used here to indicate that interchannel coupling is not responsible for the observations. To see this, let’s turn our attention to Fig. 6.6, which shows the (010)/(000) and (001)/(000) ratios plotted together and scaled to each other. The shapes of the two curves are identical within the experimental scatter; and this is strong experimental evidence that the photoelectron mediated mechanism is responsible for the intensity in the two forbidden transitions. If Herzberg-Teller coupling were responsible for creating these modes, each of them would be borrowing its intensity from a different electronic state, and one would expect that the electronic states from which they were borrowing oscillator strength would not have peaks in exactly the same place. (It is possible, but not likely.)

The vibrational mode-specificity observed in Fig. 6.4 alludes to the character of the trapped electron. Specifically, we can take a cue from some previous studies on N$_2$O 7σ$^{-1}$ photoionization. In those studies, the (100)/(000) ratio was extremely dependent on energy, while the (001)/(000) curve was essentially constant with energy.
Theoretical studies by Braunstein and McKoy\textsuperscript{119,120} provided a very simple and intuitive explanation for that observation, namely, that the trapping of the continuum electron for that system mimicked a diffuse $\sigma$ orbital that extended to the periphery of the molecule, i.e., the photoelectron was localized along the molecular axis, but not associated with a specific bond of the molecule. This was a matter of some contention during this period, and much literature was devoted to an interesting debate on precisely this point.\textsuperscript{5,6,38,99,121} The key point resulting from the current study is that the sensitivity is exactly the opposite of what was observed previously. Specifically, the (001)/(000) ratio is extremely energy-dependent, while the (100)/(000) curve is constant as a function of energy. So, it might be reasonable to suppose that the localization is quite different than what was observed previously.

One model of shape resonant wavefunction localization which is consistent with the current observations is that the photoelectron is localized along the bonds, \textit{but is concentrated in the regions between the bonds}. The asymmetric stretch actually distorts the individual bond lengths more than the symmetric stretch\textsuperscript{22}, so one would expect that the asymmetric stretching ratio would be the one to undergo more pronounced non-Franck-Condon behavior.

It is well understood that the $5\sigma_u \rightarrow k\pi_g$ shape resonance at $h\nu_{\text{exc}} \approx 21$ eV has electron density away from the molecular axis. That is why there are no vibrational motions that are sensitive to this shape resonance. This does not explain the mode specific behavior at $h\nu_{\text{exc}} \approx 42$ eV. The wave function evolves at higher energies such that the density is no longer trapped away from the molecular axis. At higher energy the trapped electron density is along the internuclear axis (in a different ionization channel.
with σ symmetry). This is consistent with the observation that the bending motion and asymmetric stretch have sensitivity but the other vibrational modes have none.

**Figure 6.6** The (010)/(000) and (001)/(000) vibrational branching ratios are plotted on top of one another. The fact that the shapes of the two curves are almost identical is strong experimental evidence that the photoelectron is responsible for mediating the intensity of these forbidden transitions.

Most of the main points provide their own summary in the preceding discussion. However, one overriding theme is worth noting. The sensitivity of the shape resonant wavefunction to alternative vibrational modes highlights that fact the photoionization dynamics can affect vibrational effects in an extremely mode-specific fashion. An important corollary to this point is that qualitative clues as to how the continuum electron is localized in this quasibound state emerge naturally from an analysis of this mode-specificity. A more specific conclusion is also worth stressing. The type of localization observed for CS$_2$ at 22 eV (d-type π function with amplitude away from the molecular axis$^{38}$) is much different from what is observed for the 42 eV resonance in CS$_2$ [σ
wavefunction with amplitude buildup along each C-S bond]. Moreover, both of these CS₂ results contrast strongly with the N₂O 7σ⁻¹ case \(^{3,4,119,120}\), as described above. The point is that there is obviously a wealth of diversity of how continuum electrons become quasibound in such systems, and these three examples discussed in this chapter may only beginning to scratch the surface of what is available for future study
CHAPTER SEVEN : N$_2$O 7$\sigma$$^{-1}$ PHOTOIONIZATION

The last two chapters have focused on the photoionization dynamics for CO$_2$ and CS$_2$. They both have the same molecular symmetry (D$_{\infty h}$), but as was discussed, their spectroscopy and photoionization scattering dynamics exhibited interesting distinctions. The last linear triatomic molecule that was studied in this dissertation research was N$_2$O. N$_2$O is different than CO$_2$ and CS$_2$ as it lacks the center of inversion symmetry. N$_2$O, like CO$_2$ and CS$_2$, has several well characterized vibrational bands. In N$_2$O, I studied the 7$\sigma$$^{-1}$ photoionization with photoelectron spectroscopy. N$_2$O has two shape resonance features, the 7$\sigma$ $\rightarrow$ k$\sigma$ at h$\nu$$_{exc}$$\approx$ 18 eV, and another 7$\sigma$ $\rightarrow$ k$\sigma$ resonance at h$\nu$$_{exc}$$\approx$ 35 eV. The shape resonance at higher energy is obscured by a nonresonant 7$\sigma$ $\rightarrow$ k$\pi$ feature at h$\nu$$_{exc}$$\approx$ 35 eV. The photoionization scattering dynamics have been the main focus of previous experimental and theoretical studies. These previous studies into the lower energy 7$\sigma$ $\rightarrow$ k$\sigma$ shape resonance showed there was mode specificity to the deviation from Franck-Condon behavior. More specifically, those previous studies demonstrated that for the localization of the quasibound shape resonant wavefunction extended over the whole molecular framework, i.e., it was not localized to a specific bond such as N-N or the N-O part of the system. N$_2$O has several vibrational modes that can be studied that were not possible owing to technical limitations in the earlier studies. This investigation extends the previous studies in a few ways. First, I will present studies on vibrational modes (e.g., bending) that were previously inaccessible. Secondly, I will present vibrational branching ratios over a greater range of energies. Thirdly, I will contrast the behavior of N$_2$O with those of the previous linear triatomic systems. It should be noted that there are no extensive theoretical calculations available for
comparison, but the present experiments will provide a more complete picture with which to investigate shape resonant ionization dynamics as well as mode-specific behavior in VUV photoionization for polyatomic systems.

7.1 Background of N₂O 7σ⁻¹ Photoionization

As with CO₂ and CS₂, the 7σ⁻¹ photoionization in N₂O has attracted a large amount of interest historically. Hence, much of the relevant background work necessary for my analysis has been done. As in the previous chapters, the details of the photoelectron spectroscopy are well established, and the energy positions of the relevant shape resonant features are well characterized. We review the most relevant studies. The photoelectron spectrum was first taken by Natalis and Collin,¹²² and Frey et al,¹²³ who reported high-resolution threshold photoelectron spectra. Dehmer and Dehmer used a supersonic expansion to reduce the initial temperature of the molecules as well as the Doppler broadening and reported a high-resolution vibrationally resolved spectrum ²⁹ of the outer valence electrons. So the valence electronic bands and the vibrational structure that are of interest have been established with high precision. In particular, there have been several studies using photoelectron spectroscopy with relatively high resolution, i.e., ca 10 meV. The significance of this is that they demonstrated that this resolution as sufficient to resolve all the features in the N₂O⁺ (A²Σ⁺) state.

Along with the fixed-energy, vibrationally resolved photoelectron experiments, there have been several energy dependent studies. The energy dependent photoionization studies have investigated both shape resonances and autoionization resonances.³⁴,²⁹,⁸³,¹²⁴,¹²⁵ Dehmer and Dehmer also ²⁹ studied the effects of autoionization resonances in all the outer valence bands N₂O. For our present purposes, the broad energy range
behavior is most pertinent, so I will focus on the $7\sigma \rightarrow \epsilon\sigma$ shape resonance, which has been the focus of extensive experimental and theoretical efforts. The first broad range study was done by Carlson et al.\textsuperscript{126} They measured the photoelectron asymmetry parameters and partial photoionization cross sections from $14 \leq h\nu_{\text{exc}} \leq 70$ eV for the four outer valence electrons. This was first measurement of the shape resonance for the $7\sigma^{-1}$ photoionization in N$_2$O. As mentioned in the introduction, there have also been studies that showed strong mode specific vibrationally resolved behavior.\textsuperscript{3,4,120} These studies exploited photoelectron spectroscopy and dispersed fluorescence over the energy range $16 \leq h\nu_{\text{exc}} \leq 25$ eV. They are particularly important because they were the first and only other studies that investigated the vibrationally resolved aspects of molecular photoionization in the region of a shape resonance for a polyatomic system. These experiments examined the energy dependence of the 001 and 100 vibrational modes. As in the previous chapter on CS$_2$, the agreement of the two different types of experiments was excellent. The mode specific behavior was dramatic, namely, the 100/000 vibrational branching ratio was sensitive to the $7\sigma \rightarrow k\sigma$ shape resonance at $h\nu_{\text{exc}} \approx 18$ eV and the 001/000 was insensitive to the same resonance. This result gave an experimental clue as to how the shape resonance was localized in the molecular framework as was discussed in the previous chapter on CS$_2$. Until these experiments and theoretical results were reported, there was considerable disagreement on how shape resonant wavefunctions were localized in molecular systems. Calculations by Braunstien and McKoy\textsuperscript{119,120}, demonstrated that shape resonances were not localized in one specific N-N or N-O bond but over entire molecular framework. The trapped electron was similar to a diffuse $\sigma$ orbital that encompasses the entire molecule. The 100 symmetric vibration
changes the end-to-end length of the molecule during the vibration, whereas the 001 asymmetric stretch does not change the overall length significantly. This provided the framework for the studies presented not only for this chapter, but for the previous chapters, as well.

7.2 Results and Discussion of N$_2$O 7σ$^{-1}$ Photoionization

The vibrationally resolved photoelectron spectra for the N$_2$O 7σ$^{-1}$ photoionization is shown for selected energies in figure 7.1. The assignments and ionization energies are as follows: the ground vibrational level ($v^+ = 000$, $E_b = 16.3915$ eV), single quantum bending excitation ($v^+ = 010$, $E_b = 16.472$ eV), the symmetric stretch ($v^+ = 100$, $E_b = 16.5601$ eV), the asymmetric mode ($v^+ = 001$, $E_b = 16.6983$ eV), two quanta of symmetric stretch ($v^+ = 200$, $E_b = 16.770$ eV), a symmetric stretch/bending combination band ($v^+ = 110$, $E_b = 16.8645$ eV), another combination band ($v^+ = 101$, $E_b = 16.8918$ eV), and the two quanta of excitation of the asymmetric stretching mode ($v^+ = 002$, $E_b = 17.0051$ eV). The unlabelled feature at $E_b = 16.930$ eV is due to an N$_2$ impurity. The assignments agree with previous photoelectron $^{3,59,122,127}$ and threshold photoelectron studies. As in the previous two chapters, the capabilities of high-resolution electron spectroscopy and undulator-based synchrotron radiation allow me to study the broad range photoionization scattering dynamics for vibrational modes that have been inaccessible to date. $^3$

The sample spectra at the selected energies of $\hbar\nu_{exc} = 18$ eV, 38 eV, 45 eV and 65 eV enable us to see that some of the vibrational branching ratios are changing substantially. This is to observe the affect of the shape resonance on the vibrational modes. For example, the (101) band is very weak at the higher energies, but is relatively
intense for the lowest energy spectrum. In order to map out the behavior systematically, vibrational branching ratios were generated from $18 \leq \nu \leq 55$ eV.

\[ h\nu = 18 \text{ eV} \]

\[ h\nu = 38 \text{ eV} \]

\[ h\nu = 45 \text{ eV} \]

\[ h\nu = 65 \text{ eV} \]

Figure 7.1 The vibrationally resolved photoelectron spectra taken of the $7\sigma^{-1}$ photoionization of N$_2$O at selected energies.

In figure 7.2 we compare the new vibrational branching ratio data to those obtained previously via dispersed fluorescence and photoelectron spectroscopy. The
agreement with the older studies is excellent. In particular, the current results corroborate that the (100)/(000) ratio is sensitive to the low energy $7\sigma \rightarrow k\sigma$ shape resonance and that the (001)/(000) ratio is not. On the other hand, the data taken at higher energies correct some experimental artifacts introduced in the earlier dispersed fluorescence studies \(^4\), as will be discussed later.

![Figure 7.2](image)

Figure 7.2 The (100)/(000) and (001)/(000) vibrational branching ratios compared to the previously reported ratios taken from Kelly \textit{et al.} \(^4\) and Ferrett \textit{et al.} \(^3\)

Figure 7.3 shows the vibrational branching ratios for the $7\sigma^{-1}$ photoionization from N\textsubscript{2}O for the energy range $17 \leq h\nu \leq 55$ eV. The curves are arranged into columns to
emphasize some similarities, and this may provide some clues as to the underlying photoionization dynamics.

![N₂O⁺(A²Σ) vibrational branching ratios](image)

Figure 7.3 The vibrational branching ratios for 7σ⁻¹ photoionization of N₂O.

The two graphs on the far left are the (100)/(000) and (200)/(000), and the shapes are quite similar. There is pronounced sensitivity of the symmetric stretching vibration to the 7σ → kσ shape resonance at hv ≈ 18 eV. While one might expect that the single quantum and double quantum excitation to display sensitivity to the same resonance, note that this was not the case for the bending excitation for the CO₂ case in Chapter 5. It also appears that there are two weaker features at higher photon energies, one at 30 eV and another at 40 eV. These are most visible in the (100)/(000) data, and there is no obvious
explanation for them. It is certainly possible that there are weaker scattering resonances
that were not obvious in the earlier studies, and additional theoretical work is necessary
to clarify this speculation.

Let’s next turn our attention to the 101/000 and 001/000 vibrational branching
ratios in the right hand column of Fig. 7.3. A close inspection of the 001/000 curve
shows that these data are relatively flat in the near threshold region (i.e., in the vicinity of
the 18 eV $7\sigma \rightarrow k\sigma$ shape resonance) as was shown previously in Fig. 7.2. On the other
hand, the 101/000 vibrational branching ratio shows considerable sensitivity to the shape
resonance at the lower energies, which might be expected because this combination band
includes the breathing motion which has been shown to be sensitive to the low energy
(18 eV) $7\sigma \rightarrow k\sigma$ shape resonance.

Theoretical studies predicted that there is another $7\sigma \rightarrow k\sigma$ shape resonance at
35 eV $^{119,120}$, as well as a nonresonant buildup of oscillator strength at the same energy
due to the $7\sigma \rightarrow k\pi$ excitation channel. In this earlier theoretical work by Braunstein and
McKoy, the nonresonant intensity was predicted to overwhelm the relatively weak
$7\sigma \rightarrow k\sigma$ shape resonance at 35 eV. There was limited investigation of this energy region
in the earlier fluorescence studies$^4$, but it was determined that there were some
experimental artifacts in the beamline used to acquire this data. As a result, the current
results shown above 30 eV are the first reliable data available for this region. In
particular, it appears that there are strong excursions in all of the branching ratios in this
region except for the two in the left hand column of Fig 7.3 described above.

If the earlier calculations by Braunstein and McKoy are accurate, it appears that
the nonresonant $7\sigma \rightarrow k\pi$ feature at $h\nu \approx 35$ eV is responsible for much of the behavior in
this region. This is hypothesized because the nonresonant oscillator strength is greater than the resonant $k\sigma$ shape resonance by approximately an order of magnitude in the calculations mentioned above. The 101/000 vibrational branching ratio also appears to have a large maximum at $h\nu_{exc} \approx 35$ eV. It is interesting to note that these maxima are very diffuse and broad, as opposed to the behavior of the curves in the central column of Fig. 7.3.

We now turn our attention to that central column of Fig. 7.3, which displays the 010/000, 110/000 and 002/000 vibrational branching ratios. All three curves display strong maxima in the vicinity of 35 eV. A few clarifications should be noted, however. First, they do not display maxima at exactly the same energy, so it is not obvious that they are all due to the same underlying mechanism. All of them are considerably narrower than the 001/000 and 101/000 curves in the right hand column discussed above. The significance of this is unclear. However, if both the center and right-hand columns display excursions due to the same root cause, then the widths might have some significance. For example, it has been explained for diatomic molecules that shape resonant widths increase as the bond lengths are decreased. There might be some analogy to this observation. Again, this is just speculation at this point.

Finally, we focus on the 010/000 branching ratio curve. It is noteworthy that this vibrational branching ratio is approaching the magnitude of an allowed vibrational excitation, as was observed to the prior bending reports for CS$_2$ and CO$_2$. Both the 110 and 010 vibrational excitations are forbidden (even in the absence of inversion symmetry), so it will be of considerable interest to see whether the photoelectron mediated mechanism which explained the previous bending behavior in CS$_2$ and CO$_2$ is
also found to be responsible for the current N$_2$O results. It is my suspicion that it is (as yet unconfirmed). If this turns out to be the case, then it may well be that this mechanism that is responsible for inducing forbidden vibrational excitations is ubiquitous, and it will be necessary to reconsider what is termed a “forbidden” transition.

These results show the utility of the vibrationally resolved experiments over a broad range, and underscore a theme of this dissertation. The quasibound photoelectron has strong mode specific behavior. Mode specific behavior could also hold clues to the mechanism responsible for the appearance of nontotally symmetric transitions. It also demonstrates the richness that photoionization can reveal given sufficiently sophisticated experimental probes. While this thesis has concentrated on simple polyatomic systems, it is clear that the ideas presented here can be extended to larger systems, and an even greater variety of interesting spectroscopic phenomena will have the likelihood of emerging.
The work presented in this dissertation presents new work on polyatomic photoionization that focuses on a unified theme. In these investigations, the broad range behavior of both allowed and forbidden vibrational modes in linear triatomic systems were studied to understand mode specific aspects of photoionization. The strategy that I employ is to probe alternative vibrational modes which are frequently affected differently following resonant ionization. Such vibrationally resolved data can be used to understand how the correlation between vibration and electron energy reveals microscopic insights into the photoelectron scattering process. Moreover, the mode specific behavior contains a wealth of information not only regarding allowed transitions, but also contains information on how forbidden transitions gain surprising amounts of intensity. A previously overlooked mechanism for the appearance of forbidden nontotally symmetric vibrations was discovered – resonantly amplified vibronic symmetry breaking. The photoelectron is responsible for the symmetry breaking which induces the excitation of nominally forbidden vibrational excitations. In a more general sense, these results also demonstrate that some fundamental spectroscopic approximations are not always valid, and can lead to surprising consequences. These data were made possible by the experimental strategy of exploiting high resolution photoelectron spectroscopy and the high brightness of third generation synchrotron radiation sources.

These results could be extended into larger molecular systems and could also have implications for core shell processes. With new experimental capabilities, such as supersonic molecular beam expansions coupled to the high brightness of third generation
synchrotron radiation sources, one could investigate whether similar phenomena arise in much larger polyatomic systems. The vibrationally resolved photoelectron spectroscopy in many cases has been well studied, albeit without photon energy dependent measurements. However, such energy dependent measurements could be performed in exactly the same way as those reported here for the linear triatomic target systems. Possible candidates include halogenated benzenes, cyclic sulfides, and halogenated thiophenes, as these systems are known to exhibit both shape resonances and Cooper minima.
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VITA

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