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NOVEL NONRESONANT AND RESONANT MECHANISMS
LEADING TO THE BREAKDOWN OF THE
FRANCK-CONDON APPROXIMATION IN PHOTOIONIZATION

A Dissertation

Submitted to 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

David Adam Hardy
B.S., The University of Akron, 2006
December 2012
Science is simply common sense at its best—that is, rigidly accurate in observation, and merciless to fallacy in logic.

-Thomas Henry Huxley
To Brittany, for your love and patience.
Acknowledgements

This is for the many people who helped and supported me in the pursuit of knowledge, and this thesis: Dr. Erwin Poliakoff, my advisor and mentor, introducing me to a new side of chemistry with patience, and support; my family for believing in me; my friend and labmate, Dr. Udaya Rodrigo; Dr. Alex Aguilar, and Bill Bates at the ALS; and most of all Brittany.
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Abstract

This thesis attempts to answer the question of how electrons interact with a molecular framework prior to and during emission through photoionization. These studies interrogate several behaviors of allowed and forbidden photoelectron transitions such as shape resonances, non-resonant intrachannel vibronic coupling as a result of Cooper minima, and chemically-induced nonresonant coupling, all of which provide new insights into correlations between the electronic and molecular degrees of freedom. Research presented in this thesis utilizes high-resolution photoelectron spectroscopy, and undulator-based synchrotron radiation at the Advanced Light Source, a synchrotron radiation source in Berkeley, California. Data are collected from near threshold to several hundred electron volts (eV) above the ionization potential. The approach is to examine how an ejected continuum photoelectron scatters and subsequently interacts with the molecular framework prior to emission. A new mechanism for mode specific vibronic coupling was also uncovered using the case of ICN ionization. As opposed to a Cooper minimum, or shape resonance produced from a bond length dependence for the continuum photoelectron as seen with N\textsubscript{2} and CO, the new mechanism results from a charge-transfer process in the initial electronic state. For both cases, the results express how a strong dependence of bond length can invalidate fundamental spectroscopic approximations. In an attempt to probe larger asymmetric systems for nonresonant behavior, gas phase nucleobases were examined for vibrational structure.
Chapter One: Introduction

The motivation behind this dissertation is to answer how an electron interacts with the molecular system prior to, and during emission. I have used photoelectron spectroscopy to probe the ionization process for molecules ionized with short wavelength radiation. More specifically, I have studied ionization of valence electrons. The specific target molecules are gas phase diatomic, triatomic, and complex asymmetric ring systems. I searched for coupling between the nuclear and electronic degrees of freedom during photoionization, as such coupling provides insights into the interaction of the photoelectron with the molecular framework as it exits. This work tests the validity of fundamental approximations for the photoionization process. This study will provide new insight to the photoionization scattering dynamics, and test the validity of fundamental spectroscopic approximations.

Let us begin with the classical image of photoionization. A photon of sufficient energy to eject an electron interacts with a free atom, or molecule. The photon is annihilated transferring its energy to the target. The molecule will then ionize. The simplified theory describes the electron as being instantaneously ejected from the system without any impediments to ionization. Well-documented cases exist for diatomic systems where a potential barrier is formed due to a strong coupling between the nuclear and electronic degrees of freedom. [1, 2] Photoionization produces both a photoion and a photoelectron. Both may be studied to understand photoionization scattering dynamics, i.e., the effect of the ejected photoelectron traverse anisotropic molecular frameworks and the resulting effects on the spectra. This thesis explores the photoelectron scattering over a relatively wide energy range to test the validity of current photoionization theory. The
work presented will explore geometry-dependent resonant effect resulting from a Cooper minimum, nonresonant effects not resulting from a Cooper minimum, and current progress on resonant effects manifested in the vibrationally resolved behavior for complex systems.

This project required the use of two experimental tools to study the photoionization dynamics over a relatively broad energy range. First, photons are produced by a tunable undulator based synchrotron radiation source coupled to a high-resolution monochromator system. The second is the use of high-resolution photoelectron spectroscopy. By combining the high flux of a 3rd generation synchrotron and the high resolving power of state-of-the-art spectrometers, we can investigate low frequency molecular vibrations, and discern between closely spaced molecular vibrations over a relatively broad range of excitation energies for polyatomic molecular photoionization.

This thesis presents my contribution to my research group’s goal of producing vibrationally resolved systems to study the global aspects of nonresonant, and resonant phenomena in the photoionization dynamics of molecular systems. The thesis will have three foci centered around the topic of broad range studies of how a photoelectron interacts with the molecular framework based on the excitation energy.

First, chapter 2 will discuss general spectroscopic theory, and provide background applicable to molecular photoionization. The Franck-Condon principle will be discussed in detail, as it is fundamental to discussing electronic transitions and subsequent vibrational structure. Other theoretical background will be discussed such as selection rules for photoionization, interchannel and intrachannel vibronic coupling, and other resonant and nonresonant effects.
Next, chapter 3 will discuss experimental facets, and applications to photoelectron spectroscopy. I will describe, in detail, synchrotron radiation, undulator based radiation, and beamline 10.0.1 at the Advanced Light Source. The instrument or endstation will be discussed including operational parameters, and sources of error.

Finally, I will discuss my experimental results. Chapter 4 describes a newly identified mechanism of photoelectron-vibrational coupling resulting not from a Cooper minimum, but rather a chemically induced, charge transfer effect. Chapter 5 presents significant advances on producing high-resolution spectra of gas phase complex asymmetric ring systems. The last two chapters will discuss present new results on continuing photoionization studies of N₂ and CO in Chapter 6, and O₂ and NO in Chapter 7.
Chapter Two: Spectroscopy Background

Quantum mechanics describes the interaction between matter and energy specifically for subatomic, atomic and molecular particles. The Born-Oppenheimer approximation (BOA) depicts a quantum system where nuclear motions of a molecule, translations, vibrations and rotations, are treated as stationary relative to the motion of the electrons, which move much more quickly.[3] As a result, we are able to separate the total wave function into a product of wavefunctions, i.e., of individual nuclear and electron wave functions. Rotational resolution is neglected for the remainder of this thesis, as it is not necessary or relevant for the studies described here.

Spectroscopy is a fundamental tool used to study quantum systems. The experiments presented in this work use a specific type of spectroscopy, photoelectron spectroscopy. Photoelectron spectroscopy is a widely used technique in many chemistry and physics laboratories [1, 4-7] for studying atomic, molecular, condensed matter, and other systems. Monochromatic radiation illuminates a target system (molecules in our studies), and the photon energy is selected so that it exceeds the ionization potential of the target and an electron is ejected from the system. The photoelectron kinetic energy distribution, angular distribution, and population of rotational, vibrational, and electronic levels are used for many purposes; specifically, such determinations are used to understand the electronic structure of molecules, as well as and the dynamics of the photoionization process.[6, 8] For this thesis, we will be mapping the photoelectron’s intensity of the valence electrons as the monochromatic light is incrementally changed. More specifically, by mapping the relative intensities of alternative vibrational transitions as a function of incident photon energy, photoelectron spectroscopy probes the coupling
between the photoelectron and nuclear motion. Such coupling can result from Cooper
minima, [8-12] vibronic coupling, [1, 8, 13-18] symmetry forbidden transitions, [1, 8, 16,
19-24] and other phenomena. [1, 11, 17, 19, 25, 26] My thesis will present observations
of a new mechanism, and new results for previously known mechanisms that deviate
from the Franck-Condon approximation. This chapter briefly outlines the Born-
Oppenheimer approximation to provide essential background. Background is also
provided on the Franck-Condon approximation, which is a central topic of my research.
Indeed, the coupling of electronic and nuclear degrees of freedom is revealed by
deviations that are exhibited as deviations from the Franck-Condon approximation.

2.1 Born-Oppenheimer Approximation

Let me commence with a brief background discussion on the Born-Oppenheimer
approximation, and some quantitative aspects of the spectroscopic background as is
significant for data analysis in later chapters. A more detailed explanation may be found
in molecular spectroscopy texts.[1, 27, 28] Equation (2.1) is the nonrelativistic, time-
independent molecular Hamiltonian operator. The contributions to the Hamiltonian are
the nuclear kinetic energy, electronic kinetic energy, nuclear-nuclear repulsion energy,
the electron-nuclear attraction energy, and the electron-electron repulsion energy.

\[
\hat{H} = \sum_{\alpha} \frac{-\hbar^2 \psi^2_{\alpha}}{2 M_n} - \sum_{l} \frac{\hbar^2 \psi^2_{l}}{2m_e} + \sum_{\alpha} \sum_{\beta \geq \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi \varepsilon_0 |R_{\alpha} - R_{\beta}|} \\
- \sum_{\alpha} \sum_{l} \frac{Z_{\alpha} e^2}{4\pi \varepsilon_0 |R_{l} - R_{\alpha}|} + \sum_{l} \sum_{j > l} \frac{Z_{l} Z_{j} e^2}{4\pi \varepsilon_0 |R_{l} - R_{j}|} \\
\hat{H} = T_N + T_e + V_{NN} + V_{eN} + V_{EE}
\]  
(2.2)
The BOA simplifies the Hamiltonian by assuming the nuclei are fixed in space relative to the electrons, and separating the electronic motion producing a new electronic Hamiltonian $\mathcal{H}_{el}$,

$$\mathcal{H}_{el} = \hat{\mathcal{H}} - \hat{T}_N - \mathcal{V}_{eN} = \hat{T}_e + \mathcal{V}_{NN} + \mathcal{V}_{ee} \quad (2.3)$$

The electronic Hamiltonian in equation (2.3) has had the nuclear kinetic energy and electron-nuclear attraction energy removed. Coulomb forces acting on the nuclei and electron are equal in magnitude, but the electrons are comparatively lighter. In consequence, electrons move much faster relative to the nuclear motion allowing the nuclei to be fixed in space. By freezing the nuclei, the purely electronic Schrödinger equation (2.4) can be solved.

$$\mathcal{H}_{el}(r,R)\psi_{el}(r,R) = E_{el}(R)\psi_{el}(r,R) \quad (2.4)$$

For a diatomic system, the subsequent electronic state, $\psi_{el}(r,R)$, and eigenfunctions, $E_{el}(R)$, will depend on the internuclear separation, $R$. The eigenfunctions are the potential energy curves. For a general polyatomic system, the internuclear separations, $R$, would be replaced with normal coordinates, $Q$, where the eigenvalues, $E_{el}(Q)$, form the potential energy surfaces. The total wavefunction is, $\psi_{ev}$, the product of the electronic and vibrational wavefunctions.

$$\psi_{ev} = \psi_{el}(r,R)\psi_{v}(Q) \quad (2.5)$$

The BOA fails when kinetic energy terms for the nuclear motion terms become comparable to the electronic terms, which is typically most important for molecules containing light nuclei, such as hydrogen. 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.
The Born-Oppenheimer approximation is essential in understanding molecular dynamics especially pertaining molecular spectroscopy, generally, and molecular photoionization, specifically. Without the separation of the nuclear and electronic degrees of freedom, a complex Hamiltonian would be need to solved, practically precluding any closed form solutions for molecular systems. When the BOA is invoked, the Hamiltonian for a nonrelativistic molecular system is greatly simplified allowing the product wavefunctions of the Schrödinger equation to be solved. The BOA does have limitations where breakdowns occur when two or more potential energy surfaces approach, or cross one another.

To use a seminal bound-to-bound state example, I will briefly describe the observation of the forbidden transition $A^1B_{2u} \rightarrow X^1A_{1g}$ transition in benzene. [29] The $A \rightarrow X$ transition is symmetry forbidden, but has been observed with moderate intensity in the near UV region. The $0 \rightarrow 0$ origin transitions are not observed, but transitions with $\Delta \nu_6 = 1$ are prominent. The $\nu_1$ ring-breathing mode is also present. Because the $\nu_1$ mode is totally symmetric, there are no symmetry restrictions on $\Delta \nu_1$. The $\nu_1$ mode always occurs in combination with an odd number of non-totally symmetric vibrations, normally $\nu_6$. The $A \rightarrow X$ transition becomes allowed by vibronic coupling and this was first explained by Herzberg and Teller.[1, 30] The Herzberg-Teller theory of vibronic coupling is a breakdown of the BOA because nuclear and electronic degrees of freedom can no longer be separated. In this instance, we must examine the total vibronic symmetry ($\Gamma^{el} \otimes \Gamma^{vib} = \Gamma^{vibronic}$). Benzene’s vibronic symmetry in the ground state is $A_{1g}$. The vibronic symmetry of the excited state is $B_{2u} \otimes e_g = E_{1u}$. If the vibrational and electronic wavefunctions are considered inseparable, then the transition moment
integral is now nonzero. By inclusion of a single quantum of vibration, the overall symmetry of the excited state is changed thus permitting the transitions. Results presented in this thesis demonstrate that the Herzberg-Teller effect is not the only conceivable justification for BOA breakdowns.

2.2 Franck-Condon Approximation Applied to Photoionization

Experiments in this thesis propose electron-vibrational coupling results in breakdowns in the Franck-Condon approximation. To help explain such mechanisms, it will be necessary to review the Franck-Condon approximation. The classical version of the Franck-Condon approximation states that electronic transitions are near instantaneous, \( <10^{-15} \text{s} \), between potential energy curves relative to nuclear motions, \( <10^{-13} \text{s} \). The Franck-Condon approximation reasons the nuclei are “frozen” during the transition forbidding the vibrational, rotational, and translational motions. As a result, the electron undergoes a vertical transition (i.e., vertical in terms of potential energy surfaces).

To appropriately depict the Frank-Condon approximation, the quantum mechanical description of an electronic transition must be described. To simplify notation, I will be describing transitions between bound states. For photoionization, excitation is from a bound state to a continuum state, but the underlying principles are the same. Let us begin with a simple diatomic system, which can be generalized into polyatomic systems. First, consider a system with an initial state \( |i\rangle \) going to a final state \( |f\rangle \) with a dipole moment operator, \( \hat{d} \). Assuming the dipole operator to be valid, this expression is valid for any transition. The dipole approximation assumes the system instantaneously experiences a uniform electric field. [1]
The dipole approximation, eq. 2.5, is central to the fact that the intensity of a given transition is proportional to the square of the transition moment integral (neglecting constants). The eigenfunctions are products of a vibrational wave function, $\chi(R)$, and electronic wave functions, $\psi(r, \theta, \phi)$, where, the electron’s position is in spherical coordinates, $(r, \theta, \phi)$, where $R$ is the internuclear separation. Notice that simply writing the total wavefunction as a product wavefunction is dependent on the BOA. For the purposes of my study, the rotational motion is ignored, and eq. 2.6 will become

$$D(i \rightarrow f) = \langle f \mid d \mid i \rangle \quad (2.6)$$

The dipole moment operator can be separated into nuclear, $d_{nuc}$, and electronic, $d_{elec}$, constituents. The total dipole operator is $d_{tot} = d_{nuc} + d_{elec}$. The matrix element will be written as

$$D(i \rightarrow f) = \langle \psi_f \chi_f \mid d_{tot} \mid \psi_i \chi_i \rangle \quad (2.7)$$

The first term is rigorously zero, even without invoking the Franck-Condon approximation. The first matrix element in eq. 2.8 can be rewritten as.

$$\langle \psi_f \chi_f \mid d_{nuc} \mid \psi_i \chi_i \rangle = \langle \chi_f \mid d_{nuc} \chi_i \langle \psi_f \mid \psi_i \rangle \rangle \quad (2.9)$$

Because the electronic wavefunctions depend parametrically on nuclear coordinates, the term, $\langle \psi_f \mid \psi_i \rangle$, cannot be separated from the nuclear integral. However, this inner matrix element is identically zero at each internuclear separation due to the orthogonality of the electronic wavefunctions (i.e., they are different solutions to the same Schrodinger equation.)
The electronic component of the dipole matrix element can be written as

\[
D(i \rightarrow f) = \langle \psi_f \chi_f | \hat{d}_{elec} | \psi_i \chi_i \rangle
\]

\[
D(i \rightarrow f) = \langle \chi_f [\psi_f | \hat{d}_{elec} | \psi_f ] \rangle \chi_i \tag{2.10}
\]

\[
D(i \rightarrow f) = \langle \chi_f [D_{elec}(R)] \chi_i \rangle
\]

\(D_{elec}(R)\) is the electronic transition dipole moment. (For photoionization transitions, this term depends on the incident photon energy through the final state continuum wave function.) The central crucial organization to the Franck-Condon approximation is as follows. If accepted that \(D_{elec}(R)\) is a slowly varying function of \(R\), then the electronic transition dipole moment can be treated as a constant and factored out of the matrix element. In the Franck-Condon framework, the variation of the electronic dipole matrix with respect to \(R\), \(D_{elec}(R)\), is neglected and replaced with an effective value, \(D_{elec}(R_0)\), where \(R_0\) is the R-centroid of the transition. The approximation of the electronic transition dipole matrix element becomes

\[
D(i \rightarrow f) = \langle \chi_f | \chi_i \rangle [D_{elec}(R_0)] \tag{2.11}
\]

The square of the transition dipole matrix is proportional to the intensity of the transition.[1]

\[
\sigma(i \rightarrow f) \propto |\langle \chi_f | \chi_i \rangle|^2 |D_{elec}(R_0)|^2 \tag{2.12}
\]

This factorization of the electronic transition dipole matrix element is the result of the Franck-Condon approximation. The value of \(|D_{elec}(R_0)|^2\) determines the strength of the transitions and is independent of the internuclear configuration. \(|\langle \chi_f | \chi_i \rangle|^2\) is the Franck-Condon factor, and is the square of the overlap integral between initial and final vibrational levels. Franck-Condon factors determine the relative intensity of the vibrational bands for a specific electronic transition, including photoionization
transitions. There is an important implication of this result. Consider the ratio of two different vibrational levels, \( \nu_{f_2} \) and \( \nu_{f_1} \), from one excited electronic transition originating from the ground vibrational level, \( \nu_i \), of the ground electronic state. A vibrational branching ratio is defined as, \( \frac{\sigma_{\nu_i-\nu_{f_2}}}{\sigma_{\nu_i-\nu_{f_1}}} \), the ratio of the relative cross-sections for two vibrational levels of an ion.

\[
\frac{\sigma_{\nu_i-\nu_{f_2}}}{\sigma_{\nu_i-\nu_{f_1}}} = \frac{|\langle \chi_{f_2} | \chi_i \rangle|^2 |P_{\text{elec}}(R_0)|^2}{|\langle \chi_{f_1} | \chi_i \rangle|^2 |P_{\text{elec}}(R_0)|^2} \tag{2.13}
\]

The dependence on the electronic transition dipole moment is the same for both vibrational levels and reduced out by the ratio.

\[
\frac{\sigma_{\nu_i-\nu_{f_2}}}{\sigma_{\nu_i-\nu_{f_1}}} = \frac{|\langle \chi_{f_2} | \chi_i \rangle|^2}{|\langle \chi_{f_1} | \chi_i \rangle|^2} = \frac{\sigma_{\nu_i-\nu_{f_2}}}{\sigma_{\nu_i-\nu_{f_1}}} \tag{2.14}
\]

The branching ratio becomes a ratio of the Franck-Condon factors. In consequence, the ratio becomes independent of the excitation energy, the incident photon energy for photoionization, and will be constant as a function of photon energy. Note that equation 2.14 hold true for diatomic and polyatomic systems. (This also assumes that the electronic wavefunctions for the final continuum state are slowly varying with electronic kinetic energy, which is usually a good approximation in the context of the work presented here.)

Nevertheless, several phenomena occur that result in the Franck-Condon approximation to fail. The most well known is a shape resonance which occurs when a centrifugal barrier temporarily traps a particle in a quasi-bound state. [31-34] For photoionization, the potential barrier enhances the photoionization cross-section near the ionization threshold forcing the ejected electron to tunnel through prior to ejection from the molecular system.[4, 35] Phenomena known to produce deviations from the Franck-
Condon approximation include shape resonances[1, 2, 13-16, 19, 22, 33, 34, 36-38],
autoionization[6, 39-41], and Cooper Minima[2, 10, 12, 20, 21, 23, 25, 26, 42]. A new
nonresonant mechanism will be presented resulting from a chemically induced charge
transfer affecting the initial state wavefunction.

2.3 Polyatomic Vibrational Selection Rules for Photoionization

Diatomcs have a few, well-defined set of rules for allowed and
forbidden electronic, and vibrational transitions, which may be generalized for triatomic
systems with a high symmetry. The approximation of the electronic transition dipole
matrix element (e.q. 2.11), and subsequently the Franck-Condon factor $|\langle \chi_f | \chi_i \rangle|^2$ (2.12)
must be a nonzero. In other words, the direct product of $\chi_f$ and $\chi_i$ must be totally
symmetric. Group theory shows a symmetric product is obtainable thus allowed if the
direct product has a totally symmetric component. For most stable molecules, the ground
state is totally symmetric ($A_1$). Because the direct product of a totally symmetric
function and a non-symmetric function produces a non-symmetric function, therefore for
any transition to occur the final state must also be totally symmetric, and any irreducible
representation other than ($A_1$).

$$\Gamma(\chi_{iA_1}) \otimes \Gamma(\chi_{f_x}) = \Gamma(\chi_{f_x}) \quad (2.15)$$

Within the framework of the Frank-Condon approximation for a single quantum, or odd
quanta of excitation $\Delta \nu = \pm 1 \pm 3 \ldots$ only symmetric stretching is allowed, and bending
and asymmetric stretching are forbidden. For even totals of quanta excitations
\[ \Delta v = \pm 2 \pm 4 \ldots \] bending and asymmetric stretching are allowed. The direct product of any excitation by itself contains a totally symmetric component.

\[ \Gamma(\chi_{\alpha}) \otimes \Gamma(\chi_{\alpha}) \subset \Gamma(\chi_{x\alpha1}) \]  

(2.16)

### 2.4 Vibronic Coupling: The Herzberg-Teller Effect

While originally developed for bound-to-bound, such as the benzene example in section 2.1, vibronic coupling is a generally accepted mechanism describing how forbidden vibrational transitions occur during photoionization. [1, 15, 18, 22, 30, 39, 43-46] The breakdown of the Born-Oppenheimer equation occurs when a single excitation of a non-totally symmetric vibration in an electronic transition obtains oscillator strength from neighboring electronic transition. While this type of breakdown does occur, we propose the Herzberg-Teller effect is not responsible for the significant breakdowns observed in our results; however, it will be necessary to for understanding the data in the later chapters.

This chapter will discuss the alternative mechanisms for non-Franck-Condon effects as explained by Herzberg. [1] Forbidden electronic transitions, referred to as “type (b)” vibronic interactions, occur in the Franck-Condon system of the “frozen” nuclei such as the classical benzene example discussed earlier. If an electronic transition is allowed for fixed nuclei, but is forbidden to contain specific vibrational excitations within the electronic transition, the transition is referred to as a “type (a)” transition. Herzberg gives no examples in his text for “type a” interactions, but covers relevant facets to photoionization processes.
The mechanism for vibronic coupling, often referred to as the Herzberg-Teller effect, will now be explained. [1, 7, 46, 47] We begin with the zeroth-order, time independent, electronic Schrödinger equation, and operator.

\[ \hat{H}_{el}^0 \psi_{el}^0 = E_{el} \psi_{el}^0 \]  

(2.17)

However, the electronic Hamiltonian depends parametrically on the vibrational coordinates requiring the total Hamiltonian to be amended for this perturbation. The unperturbed Hamiltonian is expanded with a power series.

\[ \hat{H}_{el} = \hat{H}_{el}^0 + \sum_i \left( \frac{\partial H_{el}}{\partial Q_i} \right)_{Q_i=0} Q_i + \cdots \]  

(2.18)

The Hamiltonian is reduced to the first term of the expansion.

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

(2.19)

By using the reduced, perturbed Hamiltonian, \( \hat{H}' \), the excited state wave, \( \psi_f^0 \), can interact with the zeroth-order, electronic state wave functions and be expanded as a perturbation series,

\[ \psi_{et'} = \psi_f^0 + \sum_{k \neq f} c_k \psi_k^0 \]  

(2.20)

with expansion coefficients,

\[ c_k = \frac{\langle \psi_k^0 | \hat{H}' | \psi_f^0 \rangle}{E_f^0 - E_k^0} \]  

(2.21)

The amount of borrowed oscillator strength is determined by the vibronic coupling matrix element, \( \langle \psi_k^0 | \hat{H}' | \psi_f^0 \rangle \). The strength of the vibronic coupling increases as the energy separation of the transitions, \( E_f^0 - E_k^0 \), decreases. Normally forbidden transitions can become allowed through this mechanism known as intensity "borrowing."
Herzberg-Teller vibronic coupling is a clear example of a Born-Oppenheimer approximation breakdown developing from a loss of separation of the electronic and vibrational degrees of freedom. Selection rules apply to the total symmetry of the transitions; therefore, the total vibronic symmetry is the direct product of the electronic and vibrational states.

\[ \Gamma_{\text{elec}} \otimes \Gamma_{\text{nuc}} = \Gamma_{\text{vibronic}} \quad (2.22) \]

This results in a normally forbidden vibrational state to be observed with the intensity dependent on the strength of the vibronic coupling.

A simple depiction of Herzberg-Teller vibronic coupling applied to a photoionization transition is presented in figure 2.1 where the electronic characteristics of the forbidden level, are similar to allowed level to which it is coupling. This is analogous to the bound-to-bound benzene example described earlier in Chapter 2.1. The \( A^1B_{2u} \rightarrow X^1A_{1g} \), transition is symmetry forbidden, but observed with moderate intensity in the near UV region.

In Fig. 2.1, the idea is that the nominally forbidden transition to the ground electronic state vibrational level becomes allowed when the vibronic coupling causes that vibronic level to borrow intensity from the vibrational level from the (allowed) excited electronic state. Herzberg-Teller vibronic coupling may also produce forbidden vibrations within an electronic level as portrayed in figure 2.1. A well-documented example was reported by Roy et al. [15] on the \( v^+ = (101) \) vibration in \( CO_2^+ (C^2\Sigma_g^+) \) state photoelectron spectrum. [14, 15, 48] Excitation of the \( v^+ = (101) \) is a forbidden, single quanta, asymmetric stretching vibration with a total vibronic symmetry of \( \Sigma_u \).
In that earlier study, vibrationally resolved photoelectron $C^2\Sigma_g^+$ spectra were recorded between $20 \leq h\nu \leq 28.5$ eV to measure the electronic angular distribution, or anisotropy parameter, $\beta$, for the ground vibrational mode $\nu^+ = (000)$, and the forbidden stretching mode $\nu^+ = (101)$. Anisotropy parameters depend primarily on the electronic character of an orbital with vibrational structure of a single band having identical angular distributions.[6] When the values were compared, the anisotropy parameters did not trend together indicating intensity was being “stolen” from a different electronic state. They compared the anisotropy parameters of $\nu^+ = (101)$ to the closest electronic state with a similar vibronic symmetry, $B^2\Sigma_u^+$, and discovered the values did trend in a similar fashion as depicted in figure 2.2. They concluded the Herzberg-Teller mechanism was
responsible for this case based on an analysis of Köppel et al. on the bending transition of ICN. [45] We will show that this interpretation is not the only explanation for the observed effects, and in many cases, is not even relevant.

![Figure 2](image.png)

Figure 2.2 Depiction of the anisotropy parameters adapted from Roy et al. [15] over the photon energy range of 20.0 to 28.5eV for $C^2\Sigma_u^+$ vibrational ground state (000), forbidden asymmetric stretch, and the $B^2\Sigma_u^+$ state. Notice how (000) does not have a similar trend to (101), but $B^2\Sigma_u^+$ does.

### 2.5 Photoelectron Mediated Vibronic Interactions

Recent experimental and theoretical studies have shown that a mechanism other than Herzberg-Teller vibronic coupling can be accountable for inducing forbidden transitions – which is a non-Franck-Condon effect, as well as other non-Franck-Condon effects. [12, 20-23, 25, 26, 38, 49-51] Previous studies, and the experimental results I discuss in later chapters have motivated additional theoretical work to support those qualitatively new mechanisms can be responsible for normally forbidden transitions, and
other Franck-Condon deviations. The theoretical aspects of this thesis were developed by Lucchese, [20, 22, 23, 38, 49, 50] and will now be summarized.

Herzberg [1] described a type (a) vibronic interaction as an electronic transition which is allowed for a fixed nuclei, but is forbidden to contain specific vibrational excitations within the electronic transition. Since nuclei are not fixed, the total eigenfunction must be considered. As long as inclusion of the vibrational part of the Born-Oppenheimer molecular wavefunction produces a nonzero dipole matrix element, the forbidden vibrational excitations may occur. Type (a) interactions are non-Franck-Condon effects that contain molecular vibrations, which lower the symmetry of the molecule. For the linear triatomic systems presented in chapter 4, it is possible to observe single quanta excitations of forbidden bending, and asymmetric stretching modes. Type (a) vibronic interactions have previously been identified in to have observable forbidden modes. [17, 18, 52, 53] The type (a) vibronic mechanism is significant because it is intrachannel in nature requiring no intensity “borrowing” from neighboring electronic levels.

The calculations for the vibronic matrix elements are comparable, but more complex than calculations for transitions between bound states. The complexity derives from the need to consider photoelectrons ejected along well-defined directions (signified by the wavevector \( \vec{k} \)), then averaging over all photoelectron ejection angles, and also averaging over all possible molecular orientations relative to the polarization vector. To begin with a simple example, consider a one-dimensional case, such as an asymmetric stretch. The intensity of a photoelectron transition is determined by the scattering matrix elements such as in the following equation.
\[ f_{f\rightarrow i}(\hat{k}, \hat{n}) = \left\langle \chi_{vi}^{(i)}(q) \middle| f(\hat{k}, \hat{n}, q) \middle| \chi_{vf}^{(f)}(q) \right\rangle_q \]  

(2.23)

\( f_{f\rightarrow i}(\hat{k}, \hat{n}) \) is the electronic amplitude. The inversions of the vibrational wavefunctions, \( \chi \), have definite symmetry with respect to the parity operator, \( q \). The electronic matrix element is \( f(\hat{k}, \hat{n}, q) \). Next, expand the electronic amplitude in the vibrational coordinate \( q \), and retain the first two terms.

\[ f(\hat{k}, \hat{n}) = F_0(\hat{k}, \hat{n}) + qF_1(\hat{k}, \hat{n}) \]  

(2.24)

\( F_0 \) and \( F_1 \) must be orthogonal to each other when integrated over all directions, \( \hat{k} \) and \( \hat{n} \), for the total cross section averaged over all orientations will be an even function of \( q \). By substituting equation (2.23) into equation (2.22), we produce the following equation.

\[ f_{f\rightarrow i}(\hat{k}, \hat{n}) = F_0(\hat{k}, \hat{n})\left\langle \chi_{vi}^{(i)}(q) \middle| \chi_{vf}^{(f)}(q) \right\rangle_q + F_1(\hat{k}, \hat{n})\left\langle \chi_{vi}^{(i)}(q) \middle| q \middle| \chi_{vf}^{(f)}(q) \right\rangle_q \]  

(2.25)

The Franck-Condon selection rule that allow transitions have even quanta of excitation, \( \nu_f - \nu_i = 2n \), arise from the first term. The second term leads to normally forbidden transitions with odd quanta of excitation, \( \nu_f - \nu_i = 2n + 1 \); which occur because the dipole amplitudes vary with the vibrations corresponding to the non-totally symmetric modes.

By expanding upon this reasoning, we will consider a two-dimensional case, such as a bending mode for linear triatomic systems. Either Cartesian coordinates, \((x, y)\), or polar coordinates, \((q, \gamma)\), may be used to describe the bending coordinates. We will begin by substitution Cartesian coordinates into equation (2.23).

\[ f_{f\rightarrow i}(\hat{k}, \hat{n}) = \left\langle \chi_{vi,x}^{(i)}(x) \chi_{vi,y}^{(i)}(y) \middle| f(\hat{k}, \hat{n}, x, y) \middle| \chi_{vf,x}^{(f)}(x) \chi_{vf,y}^{(f)}(y) \right\rangle \]  

(2.26)

The electronic amplitude expansion from equation (2.24) becomes
\[ f(\kappa, \eta, x, y) = F_0(\kappa, \eta) + xF_x(\kappa, \eta) + yF_y(\kappa, \eta), \quad (2.27) \]

and is substituted into equation (2.26) to give
\[
f_{fi}(\kappa, \eta) = F_0(\kappa, \eta) \left\langle \chi_{vi,x}^{(i)}(\alpha) \mid \chi_{vf,x}^{(f)}(\alpha) \right\rangle x \left\langle \chi_{vi,y}^{(i)}(\eta) \mid \chi_{vf,y}^{(f)}(\eta) \right\rangle y
+ F_x(\kappa, \eta) \left\langle \chi_{vi,x}^{(i)}(\alpha) \mid \chi_{vf,x}^{(f)}(\alpha) \right\rangle x \left\langle \chi_{vi,y}^{(i)}(\eta) \mid \chi_{vf,y}^{(f)}(\eta) \right\rangle y \quad (2.28)\]
\[
+ F_y(\kappa, \eta) \left\langle \chi_{vi,x}^{(i)}(\alpha) \mid \chi_{vf,x}^{(f)}(\alpha) \right\rangle x \left\langle \chi_{vi,y}^{(i)}(\eta) \mid \chi_{vf,y}^{(f)}(\eta) \right\rangle y.
\]

In polar coordinates, equation (2.23) becomes
\[
f_{fi}(\kappa, \eta) = \left\langle \chi_{vi,l_i}(q) e^{i\ell_i \lambda} \mid f(\kappa, \eta, q, y) \right\rangle \left\langle \chi_{vf,l_f}(q) e^{i\ell_f \lambda} \right\rangle_{q,y} \quad (2.29)\]

The electronic amplitude expansion from equation (2.24) becomes
\[
f(\kappa, \eta) = F_0(\kappa, \eta) + q e^{iy} F_1(\kappa, \eta) + q e^{-iy} F_{-1}(\kappa, \eta) \quad (2.30)\]

Just as with the one-dimensional case, the \( F \) functions, where \( F_1 = \frac{F_x + F_y}{2} \), and \( F_{-1} = \frac{F_x - F_y}{2} \), must be orthogonal to \( F_0 \), or each other. By substituting equation (2.30) into (2.29), the transition amplitude is
\[
f_{fi}(\kappa, \eta) = F_0(\kappa, \eta) \left\langle \chi_{vi,l_i}(q) \mid \chi_{vf,l_f}(q) \right\rangle \delta_{li,lf}
+ F_1(\kappa, \eta) \left\langle \chi_{vi,l_i}(q) \mid q \chi_{vf,l_f}(q) \right\rangle x \delta_{li,lf+m+\mu} \quad (2.31)\]
\[
+ F_{-1}(\kappa, \eta) \left\langle \chi_{vi,l_i}(q) \mid q \chi_{vf,l_f}(q) \right\rangle x \delta_{li,lf+m+\mu}.
\]

For both one- and two-dimensional motions, the first term leads to the allowed Franck-Condon transitions, and the following terms, \( F_1 \) and \( F_{-1} \), lead to the non-Franck-Condon forbidden transitions. The two-dimensional symmetry is controlled by the motion around the \( z \)-axis, which is indicated by the Kronecker deltas in equation (2.31). Based on the
equivalence of equations (2.25) and (2.31), it is apparent that vibronic transitions are solely determined by the symmetry of the one-dimensional bending mode.

![Diagram](image)

Figure 2.3 Example of potential energy diagram for the intrachannel photoelectron mediated vibronic coupling mechanism.

The fundamental development of this mechanism is that it invokes no interchannel coupling either implicitly, or explicitly. The outgoing photoelectron solely contains intensity in the excitation for non-totally symmetric vibrations. Figure 2.3 contains a simple diagram for the photoelectron mediated vibronic coupling mechanism. However, this mechanism depends on the electronic matrix element changing as the non-totally symmetric coordinate is varied, i.e., the $F_{\pi 0}$ term in equations (2.25) and (2.31). This is another way of stating that the electronic transition matrix element depends on changes in geometry, which negates the central premise of the Franck-Condon
approximation. Sources of the dependence are discussed in the following section, but the key point is that sensitivity of the photoelectron ejection dynamics to molecular geometry provide a basis for inducing nominally forbidden vibrational transitions in photoionization.

2.6 Breakdown Mechanisms of the Franck-Condon Approximation

Franck-Condon breakdowns in photoionization result from a strong dependence on the internuclear distance, $R$; in equation (2.10). In consequence, equation (2.11) will not work. A fixed dipole matrix element becomes invalid, and the change in the geometry must be considered. Several examples of non-Franck-Condon phenomena have been reported in literature including shape resonances, autoionization, and Cooper minima, and will be discussed below. One novel phenomenon resulting from an initial state charge transfer to date will be discussed briefly with more detail given in Chapter 4.

2.6.1 Shape Resonance

In molecular photoionization, a shape resonance is a single-electron continuum-state phenomenon. A quasi-bound state is formed when the photoelectron is trapped by a potential barrier created by a combination of Coulomb screening and centrifugal forces. The process occurs on the edge of the valence orbital radii where the attractive and repulsive forces are equal. The result of this potential barrier is that the photoelectron is temporarily trapped, and it transverses the system several times before leaving the molecular core by quantum-mechanically tunneling through the potential barrier. The term “shape resonance” comes from the dependence on the shape, height, and width of the potential energy barrier reflecting electronic configurations, molecular geometry, and
other forces. There are several consequences to this trapping. Since the quasi-bound state is formed inside the potential barrier (i.e., electron density for the final state is enhanced in the region of the initial state orbital from which the electron is ejected), the dipole matrix element is enhanced, leading to a peak in the photoionization cross-section. [4, 6, 34-37, 54, 55] Other effects are also possible such as changes in the photoelectron angular distributions.[4, 35, 56] While shape resonances are not the central theme of this thesis, I will address how the photoelectron becomes localized in a polyatomic system.

Shape resonances often produce deviations from Franck-Condon behavior. There exist two rationales on why Franck-Condon deviations occur; they are qualitative statements that are equivalent. The first explanation is that times scale of the photoelectron escape becomes comparable to the period of the vibrational motion. The electronic and vibrational degrees of freedom become entangled, and invalidate equation (2.10). The second explanation is that the shape of the potential energy barrier, and the effectiveness in trapping of the photoelectron within the molecular geometry, depends on geometrical distortions due to vibration. [35, 54, 55, 57-59] The key point is that the interaction between the electronic and nuclear degrees of freedom results in Franck-Condon breakdown.

The potential barrier in photoionization can be represented schematically by a one-dimensional barrier affecting an unbound wavefunction in the vicinity of a quasibound state. [5, 37, 54, 60] A potential energy well is shaped on the inside by a partial screened nuclei of the molecular ion. This results in a highly anisotropic shape, which overlaps the molecular charge distribution. A potential barrier is created by the repulsive Coulomb potential \(\approx -r^{-1}\) competing with the attractive centrifugal
forces($\approx +r^{-2}$). The process occurs on the edge of the valence molecular charge
distribution where the attractive and repulsive forces approach are equal, i.e., near the top
of the barrier. The barrier in figure (2.4) is comparable to a one-dimensional barrier from
quantum mechanics while the realistic the barrier is much more complex than portrayed
in that it is geometry dependent. The horizontal axis is the photoelectron distance from
the center of the molecule. Figure (2.4) depicts the effect of the potential barrier for three
different continuum photoelectron energies.

![Diagram showing the effect of a potential barrier on a photoelectron wavefunction]

Figure 2.4 Schematic of the effect of a potential barrier on a photoelectron wavefunction
around a quasibound state. The horizontal axis represents the distance of the electron
from the center of the molecule. Adapted from refs. [5, 35, 60]

For a shape resonance to occur, the photoelectron must be in a “Goldilocks energy
zone.” When the energy of the photoelectron is greater than the resonance energy, the
electron is essentially an eigenfunction of the outer potential, and is no longer a bound state. When the energy of the photoelectron is less than the resonance energy, the inner well of the potential cannot support a bound state, and the photoelectron tunnels out. At the resonance energy and conditions, the inner well supports a quasibound state, and the wavefunction is enhanced increasing the photoionization cross-section. The wavefunction would exhibit an exponential decay in the barrier. If the barrier was extended to $r \to \infty$, a real bound state would exist near this energy. [33, 34, 36, 37] The key point about a shape resonance is that the nature of the barrier depends sensitively on changes in molecular geometry, and this dependence is what results in Franck-Condon breakdown.

The Franck-Condon approximation breaks down as a result a strong dependence on internuclear distance, and of the nature of a shape resonance. The quasibound state, produced by the potential barrier is sensitive to changes in the molecular geometry, i.e., internuclear distance in the case of a diatomic system. The induced localization of the electronic wavefunction has implications for photoionization, which will be examined as part of this thesis.

Shape resonances in diatomic molecules have been extensively studied. [5, 31-33, 36, 37, 49, 61-66] The remainder of this section will be devoted to the well known, and documented $\sigma_u$ shape resonance in the $N_2^+ 3\sigma_g \to k\sigma_u$ ionization channel.[34, 36, 37] Non-Franck-Condon behavior stems from the geometry dependence of quasi-bound state created on the edge of the valence orbital radii by a potential barrier. Figure 2.5 contains calculated results for the $\sigma_u$ shape resonance. The left frame shows calculated photoionization cross-sections ($\sigma$) for $N_2^+ 3\sigma_g (v_1 = 0)$ for different R-fixed values indicated by the dashed lines. The solid line in the left frame is the R-averaged value;
which is equivalent to a vibrationally unresolved electronic level. Clearly, the resonance position, strength and width are sensitive to $R$. As the bond length increases the resonance shifts to a lower kinetic energy, narrows, and increases in intensity. It is obvious that nuclear motion has a strong influence on the resonance profile. In vicinity of a shape resonance, the electronic transition moment varies rapidly with $R$ indicating a strong coupling between electronic and nuclear coupling.

![Figure 2.5](image)

Figure 2.5 The left frame shows calculated photoionization cross-sections, $\sigma$, for $N_2^+ 3\sigma_g (\nu_1 = 0)$ for fixed $R$-values indicated by the dashed lines. The solid line is the $R$-averaged, vibrationally unresolved value. The right frame shows the $R$-weighted results for the $\nu^+ = 0 \rightarrow 2$ vibrational levels. Adapted from refs. [34-36, 49, 54]

The right frame shows the $R$-weighted theoretical results for the $\nu^+ = 0 \rightarrow 2$ vibrational levels. Small variations in the internuclear separation, $R$, significantly shift the balance between attractive coulomb, and repulsive centrifugal forces that form the potential barrier. The implication of figure 2.5 is the underlying photoionization dynamics of shape resonances can be examined by studying the how non-Franck-Condon behavior is expressed. One aspect for my thesis will involve examining shape resonances, and other non-Franck-Condon phenomena in diatomic systems. This work will expand
upon the subject, and examine continuum photoelectron shape resonances in polyatomic systems that were previously inaccessible because of technical limitations.

2.6.2 Autoionization

Autoionization is a resonant phenomenon occurring in most photoionization spectra. [6] Unlike shape resonances produced by direct ionization, autoionization is a multichannel, indirect process. Specifically, autoionization occurs when a bound state in one channel lies in the continuum of another channel. [1, 6] For example, electronic autoionization occurs when an electron excited from an inner valence orbital decays into the continuum of an outer valence electron channel. This requires a two electron process to occur, and thus is classified as a multichannel process, rather than a single channel process. Typically, autoionization processes arise very near the ionization threshold, and are very narrow (FWHM of 0.05eV or less). [49] For this reason they will not be examined in this work outside of this section because their non-Franck-Condon effects are so localized, spectroscopically-speaking. Unlike shape resonances produced by direct ionization, autoionization is a multichannel, indirect process. Because autoionization is an indirect process, the ejected photoelectron contains information about the initial, final, and intermediate wavefunction. Autoionization phenomena have been studied more extensively in comparison to shape resonances. A majority autoionization are the results of Rydberg states of series converging on inner ionization levels. As opposed to a shape resonance where the photoelectron tunnels out of a potential barrier, the electron is excited to a super excited intermediate, $M^*$. 

$$ M + h\nu \rightarrow M^* \rightarrow M^+ + e^- \quad (2.32) $$
The emitted electron can interfere and distort the direct ionization photoelectron spectrum through electronic, and vibrational autoionization processes. Vibrational autoionization occurs when excess vibrational energy of the intermediate is converted into electronic energy resulting in ejection of a low energy electron from a Rydberg level. Unless the excitation energy corresponds to a molecular resonance, vibrational autoionization will occur with a relatively weak intensity as to not effect on the direct photoelectron spectrum. Figure 2.6 presents a simple autoionization example of how a super excited intermediate may contribute to the population of an otherwise forbidden vibrational level of an ionic state.

Figure 2.6 Example of potential energy diagram for autoionization process. Adapted from ref. [6]
Electronic autoionization is a two-electron process where an inner shell electron is excited to a Rydberg state, the excited intermediate then relaxes, and the excess excitation energy ejects a valence electron. The normal photoelectron spectrum is greatly influenced by electronic autoionization as the process excites ionic states in different proportions compared to direct photoionization.

2.6.3 Cooper Minima

A Cooper minimum is a nonresonant photoionization phenomenon that can produce non-Franck-Condon behavior, excursions in the cross sections, asymmetry parameters, and other dynamical variables. [12, 20, 21, 25, 26, 42, 50, 67-69] They were originally discovered in cross-section experiments performed on alkali metal vapors, which revealed broad minima as a function of energy. [70] J.W. Cooper first explained the phenomena for atomic systems as a cancelation in the radial dipole length matrix element that resulted from opposite contributions from the positive and negative lobes of the initial state radial wave function when the photoelectron energy is tuned to a specific value. [42] If one separates the angular and radial coordinates, [71] then integrates over the angular coordinates, one is left with the radial dipole length matrix element, which can be written as

\[ R_{l\pm 1}(\varepsilon) = \langle \psi_{\varepsilon, l \pm 1}(r)|r|P_{nl}(r) \rangle. \]  

(2.33)

\( P_{nl}(r) \) and \( P_{\varepsilon, l \pm 1}(r) \) are the bound and final state radial wave functions. The r-weighted overlap integral has opposing contributions from the positive and negative lobes of the bound state wavefunction. Due to the possibility of radial nodes in the bound state wavefunctions, such as a 2s or 3p orbital, the matrix element can change sign as the
photoelectron energy is scanned. The change in sign results in the dipole matrix radial element going through a zero, which can lead to a minimum in the cross section.

Cooper showed that the cancellation was a general effect.[42, 72, 73] Consider the examples of the valence photoionization of neon and argon.[42, 72] Figure 2.7 contains the initial radial state wavefunctions (Ne 2p in top frame, Ar 3p in middle frame) and d-wave radial wave functions a near-threshold ionization-continuum electron. Through calculating the dipole integral, neon is clearly positive, and argon is negative.

Figure 2.7 The outer subshell radial wavefunctions and d waves at zero kinetic energy for Neon and Argon. The horizontal axis is in units of Bohr radius ($a_0$). Adapted from ref. [42, 72].

By increasing the photoelectron energy and in turn, the kinetic energy of the continuum electron, the wavelength of the d-wave will decrease and “move-in” toward the origin. While the continuum d-wave functions are similar for neon and argon, the neon
(2p), and argon (3p) initial state wavefunctions are quite different. As the overlap changes, neon will remain positive with the d-wave lacking significant negative intensity. The d-wave for argon will have a significant positive contribution to the radial matrix element. Figure 2.8 contains the $R_{l+1}$ integral plotted as a function of kinetic energy. At approximately 25eV, the integrand for argon becomes zero and changes signs as the energy is further increased. This represents the conditions for a Cooper Minima, or a Cooper “zero”. For atomic species, when the negative lobe in the bound state wave function leads is completely cancelled by the final state wavefunction leading to a change in sign of the radial matrix elements as a function of excitation energy.

![Figure 2.8](image.png)

Figure 2.8 The matrix elements for the $p \rightarrow d$ transitions in Neon, and Argon. Adapted from ref. [42].

When other excitation channels are available, the Cooper “zero” becomes a Cooper “minimum” as a result of the other channels potentially contributing to the cross-section, but not have a cancellation effect. Cooper minima can affect oscillator strength, [72-74] angular distributions [63, 69, 75] over broad energy ranges for atomic and molecular systems. [9, 10, 12, 23, 24, 38, 43, 67, 68, 76-80]
Cooper minima can also occur in molecules, and studies of the \( N_2^+ 2\sigma_u^{-1} \) vibrational branching ratios have shown that the internuclear separation significantly shifts as the result of a Cooper minimum. [12, 78, 79] A breakdown of the Franck-Condon approximation was observed due to the sensitivity of the electronic transition dipole moment to the changes in the internuclear separation. This specific case as well as other diatomic molecules will be covered in more detail in Chapter 6. The consequence of the study is the need to investigate polyatomic systems for influences on the vibrational photoionization dynamics by Cooper minima.

2.6.4 Initial State Charge Transfer

An initial state charge transfer is a novel, nonresonant mechanism of photoelectron-vibrational coupling of a polyatomic system. The previously stated mechanisms result in a deviation in the continuum state wave function. The charge transfer effect influences the electronic character of the initial state wavefunction. Specifically for ICN, the result is a chemically induced charge transfer from iodine to the CN moiety resulting in a change of the C-N bond length. As with Cooper minima, a broad-ranging (i.e. 20-200eV), mode-specific Franck-Condon breakdown was observed due to the sensitivity of the electronic transition dipole moment to the changes in the internuclear separation. Results will be discussed in Chapter 4.
Chapter Three: Experimental

3.1 Introduction

The research presented in this thesis utilized high-resolution photoelectron spectroscopy coupled to a high brightness undulator based synchrotron radiation at the Advanced Light Source, Berkeley, CA. combined with a high-resolution hemispherical electron analyzer. The method employs a simple strategy; incrementally increasing the photon energy, and record photoelectron spectra as the incident energy is varied. This has the effect of controlling the energy of the ejected photoelectrons. By tuning the kinetic energy, we can study continuum effects in regions of interest, such as a shape resonance over a relatively limited energy region, or a non-resonant feature over several hundred eV. This chapter will explain the experimental instrumentation used to perform molecular photoionization over relative wide photon energies. Sources of synchrotron radiation, a synchrotron beamline, and high-resolution electron energy analyzers will be discussed.

3.2 Molecular Photoionization

The basic process of molecular photoionization is that a photon with an energy that exceeds the ionization potential is absorbed emitting a photoelectron, and leaves behind a residual photoion. Other processes may also occur such as fluorescence and Auger decay. For the research reported in this thesis, only the basic photoionization process was investigated. Specifically, vacuum ultraviolet (VUV) radiation was used to study the photoionization dynamics of valence levels of molecular systems.

The main advantage of using direct photoionization is that the interpretation of the process and subsequent data analysis are relatively straightforward, owing to the
conservation of energy. The energy of the photon, $h\nu$, is imparted on the molecule. Through the conservation of energy, an electron is ejected with a kinetic energy, $E_k$, given by equation (3.1). Because the binding energy, $E_b$, is a constant, the equation can be differentiated as seen in equation (3.2).

$$E_k = h\nu - E_b \quad (3.1)$$

$$\delta E_k = \delta (h\nu) \quad (3.2)$$

The implication is that the kinetic energy is directly dependent on the photon energy. As a result, the kinetic energy of the photoelectron can be scanned using tunable monochromatic light, such as that which emerges from a monochromator beamline at a storage ring. The consequence of this technique is the resolution is limited by the bandwidth of the light source; in the case of synchrotron radiation sources, a practical consequence is that the photon bandwidth can exceed 100 meV at higher photon energies used in our studies. With the vibrational spacing of complex molecules being less than 20 meV, this can become quite problematic.

### 3.2.1 Photoelectron Spectroscopy

Photoelectron spectroscopy is the study of photoelectrons’ energies, abundances, and angular distributions emitted from occupied molecular orbitals. [6] The experimental technique allows the selective study of individual molecular orbitals. By recording the intensity, and kinetic energy of the photoelectron, the scattering process for each target system can be probed. Because photoionization is a direct process, the identification of electronic and vibrational structure photoelectron spectrum is relatively straightforward procedure.
Photoelectron spectroscopy has a limitation that can be very challenging for the experiments that are the focus of my work; namely, the resolution of the spectra is limited by the source bandwidth. In order to perform my research, it was essential to employ synchrotron radiation with the technical capabilities to generate high-resolution photoelectron spectra over a broad range of energies. Historically, high-resolution photoelectron spectroscopy experiments were performed with resonance lamps and lasers.\cite{13, 14, 16-18, 29, 81-91} Recently, zero electron kinetic energy studies (ZEKE) have made meaningful advances in producing vibrationally resolved photoelectron spectra (<10meV), \cite{85, 92, 93} but are restricted to threshold studies. Synchrotron radiation from older sources has also been used to study photoelectron spectra, but has been limited by the broad source bandwidth. New and retrofitted synchrotrons have been making use of high brightness insertion devices coupled with high-resolution optics to produce a significant amount of photons with a narrow bandwidth (<1meV possible). \cite{94, 95} Aforementioned advances have made studying low frequency vibrations of polyatomic systems, such as ICN and nucleobases, over a range of excitation energies possible.

3.3 Synchrotron Radiation and Beamline 10.0.1 at the Advanced Light Source

This section will give a brief introduction to synchrotron radiation, components of a 3\textsuperscript{rd} generation electron storage ring, and operational parameters. Special attention will be given to insertion devices, and operational characteristic as they pertain to Beamline 10.0.1 at the Advanced Light Source (ALS), Berkeley, CA.
3.3.1 Introduction to Synchrotron Radiation

Synchrotron radiation is light emitted by charged particles, such as electrons, accelerated radially at ultrarelativistic velocities. Larmor first described the non-relativistic treatment of electromagnetic radiation produced by accelerated particles in the 1890’s. In 1946, Schwinger used a relativistic approach to describe the energy loss mechanism of electrons in storage rings. [97, 98] General Electric fabricated the first synchrotron in 1946. [99] After 10 years of characterizing synchrotron radiation, the first synchrotron experiments were performed by Tomboulian and Hartman in 1956 in the far ultraviolet/soft X-ray region (>20eV). [100] First-generation synchrotrons were initially designed for accelerator physics experiments, i.e. particle collision. The energy loss from synchrotron radiation at the “bending” magnets was initially considered a “parasitic” waste of energy. [94, 95] Second-generation synchrotrons were designed with the primary goal of producing synchrotron radiation from the bending magnets, and dedicated storage rings were eventually constructed. The first 2nd-generation synchrotron, Synchrotron Radiation Source, was built in 1970 at Daresbury Laboratory, Cheshire, England. [95] Modern day third-generation synchrotrons, such as the Advanced Light Source, were designed and built to optimize the brightness of the radiation. This is accomplished by having long straight sections between bending magnets where specially designed insertion devices can be used to produce high flux, low divergence radiation over tunable, narrow energy ranges. Radiation from bending magnets and insertion devices will be discussed in greater detail in the following section. My research utilizes the light from an insertion device, U100 undulator, at Beamline 10.0.1 in the Advanced Light Source in Lawrence Berkeley Laboratory, Berkeley, CA. Presently, there are
approximately 70 second- and third-generation synchrotrons worldwide either operating, or under construction. [101]

3.3.2 Light Sources

Synchrotron radiation is electromagnetic radiation conically emitted by charged particles moving at ultrarelativistic velocities subjected to a circular orbit. The theoretical description is outside the reach of this thesis, but may be found in classic texts.[94, 102, 103] However, it will be necessary to define some common terms used when describing synchrotron radiation such as flux and brightness. The photon flux, \( \mathcal{F} \), is useful in characterizing the source strength. Equation 3.2 describes photon flux as the number of photons per unit time, emitted into a solid angle, \( \Omega \).

\[
\mathcal{F} = \int \frac{d^2 \mathcal{F}}{d \theta d \psi} d \Omega = \int \frac{d^2 \mathcal{F}}{dxdy} dxdy \quad (3.2)
\]

\( \theta \), and \( \psi \) are the horizontal and vertical angles that define the solid angle, and \( x \) and \( y \) are Cartesians coordinates that define the area of the source moving in the \( z \)-axis. Brightness, \( \mathcal{B} \), is defined by equation (3.3) is the phase-space density of the photon flux along the \( z \)-axis.

\[
\mathcal{B} = \frac{d^4 \mathcal{F}}{d \theta d \psi dx dy} |_{0} \quad (3.3)
\]

To describe a high brightness source with a low bandwidth such as produced by an undulator source; the term spectral is used when describing flux and bandwidth. Typical units for spectral flux, \( \mathcal{F}_s \), and spectral bandwidth, \( \mathcal{B}_s \), are given as

\[
\mathcal{F}_s = \frac{\text{number of photons}}{(0.1\% \text{ bandwidth})dt} \quad (3.4)
\]

\[
\mathcal{B}_s = \frac{\mathcal{F}_s}{d \Omega dx dy}. \quad (3.5)
\]
The spectral flux is the number of photons in a 0.1% fractional bandwidth $h\nu$ per unit time. The spectral bandwidth is the $F_s$ over the solid angle, $d\Omega$, at a defined point in space down from the source on-axis.

### 3.3.2.1 Bending Magnet Radiation

The first sources of synchrotron radiation used for scientific applications originated from the bending magnets of 2nd generation sources used to steer the charged particles around the storage ring. This section will describe the on-axis density of flux, photon flux, and total radiated power for bending magnets with application at the ALS.

The angular density of radiation emitted from relativistic electrons accelerated by bending magnet can be defined as

$$
\frac{d^2\mathcal{F}_b(\omega)}{d\theta d\phi} = \frac{3\alpha}{4\pi^2}\gamma^2 \frac{\Delta \omega}{\omega} \frac{l}{e^2} \gamma^2 (1 + X^2)^2 \times \left[ K_{2/3}(\xi) + \frac{x^2}{1+x^2} K_{1/3}(\xi) \right]
$$

(3.6)

where $\alpha = e^2/\hbar c$, $l$, and $e = 1.602^{-19}$ coulombs are the fine-structure constant, beam current, and electron charge respectively. $X = \gamma \psi$, where $\gamma = E_e/m_0c^2$, $E_e$ is the energy of circulating electrons in the storage ring, and $m_0$ is the mass of a resting electron, and $c$ is the speed of light in a vacuum. $K_{\lambda}^{2}(\xi)$ are modified Bessel functions of the second kind [104] where $\xi = \gamma (1 + X^2)^{3/2}/2$, and $\gamma = \omega/\omega_c = \varepsilon/\varepsilon_c$. The critical frequency, $\omega_c$, is a parameter used to characterize the bending magnet radiation by dividing the emitted power into equal halves, and is defined as

$$
\omega_c = \frac{3\gamma^2c}{2\rho}.
$$

(3.7)

The instantaneous radius of curvature, $\rho$, critical wavelength, $\lambda_c$, and critical energy, $\varepsilon_c$, are given using the most common units.

$$
\rho(m) = 3.336 \frac{E_e(\text{GeV})}{B(T)}
$$

(3.8)
\[ \lambda_c (\text{nm}) = \frac{1.864}{|E_e (\text{GeV})|^2 B(T)} \]  \hspace{1cm} (3.9)

\[ \varepsilon_c (\text{keV}) = 0.06650 [E_e (\text{GeV})]^2 B(T) \]  \hspace{1cm} (3.10)

\( B(T) \) is the magnetic field of the dipole bending magnets in Tesla. A bending magnet is also characterized by radiated power, \( P \), which is the energy emitted per unit time given in equation (3.11), and in commonly used units in equation (3.12).

\[ P = \frac{2e^2 c \gamma^4}{3 \rho^2} = \frac{2e^2 c E_e^4}{2 \rho^2 (m_0 c^2)^4} \]  \hspace{1cm} (3.11)

\[ P_{\text{tot}} (\text{kW}) \approx 0.0265E_e^4 (\text{GeV}) B(T)i(\text{mA}) \]  \hspace{1cm} (3.12)

Figure 3.1 Plot of the brightness, and photon flux from a typical 1.27 T bending magnet at the Advanced Light Source. [105]

For the Advanced Light Source operating under normal conditions at \( E_e = 1.90 \text{ GeV} \) and 500 mA with a typical 1.27 T normal bend, and 5 T super bend magnets give the following values.
\[ \gamma = \frac{E_e}{m_0c^2} = 3720 \]

\[ \rho_{1.3}(m) = 3.336 \frac{E_e(\text{GeV})}{B(T)} = 5.0 \text{ m} \quad \rho_5(m) = 1.25 \text{ m} \]

\[ \lambda_{c,1.3}(\text{nm}) = \frac{1.864}{[E_e(\text{GeV})]^2 B(T)} = 0.407 \text{ nm} \quad \lambda_{c,5}(\text{nm}) = 0.103 \text{nm} \]

\[ \varepsilon_{c,1.3}(\text{keV}) = 0.06650 [E_e(\text{GeV})]^2 B(T) = 3.05 \text{ keV} \quad \varepsilon_{c,5}(\text{keV}) = 12.0 \text{ keV} \]

\[ P_{\text{tot,1.3}}(\text{kW}) \approx 0.0265 E_e^3 (\text{GeV}) B(T) i(mA)) = 115 \text{ kW} \quad P_{\text{tot,5}}(\text{kW}) = 454 \text{ kW} \]

### 3.3.2.2 Insertion Devices

Insertion devices consist of a periodic array of magnetic poles designed to produce an oscillatory motion of the electrons perpendicular to the electron beam in the straight sections of synchrotrons. Each oscillation of the electrons produces synchrotron radiation in a similar fashion to the bending magnets discussed earlier. The results of the oscillations in the same plane produce a concentrated radiation along the axis of the insertion device that can be linearly or circularly polarized. The result is that undulator radiation is both more intense, and more monochromatic than radiation emerging from a bending magnet. A cartoon image in figure 3.2 illustrates how an insertion device works.

Two types of insertion devices exist: wigglers and undulators. Wigglers and undulators are similar in general design, but vary one key value, the K parameter.

\[ K \equiv \frac{eB \lambda_u}{\pi n mc} = \delta \gamma \approx 0.9337 B(T) \lambda_u (cm) \quad (3.12) \]

\( B \) is the magnetic field, and \( \lambda_u \) is the magnet period. The K parameter is proportional to the maximum deflection angle, \( \delta \), the electron undergoes in the insertion device.
Figure 3.2 Simple illustration of how an insertion device produces synchrotron radiation. The oscillations are in the plane of the magnetic field indicated by the arrows on the permanent magnets.

Radiation is emitted in a narrow half cone based on $\gamma$, and the number of oscillation periods, $N$, commonly referred to as the central radiation cone.

\[ \theta_{cen} = \frac{1}{\gamma \sqrt{N}} \quad (3.13) \]

For $K \gg 1$, the deflection angle is greater than the central cone resulting in a minimal amount of interference effects caused by electronic oscillations within the central radiation cone. The radiating power is $2N$ greater compared to a bending magnet with a similar flux/brightness curve. For this particular case, the insertion device is called an undulator.

When $K \leq 1$, the interference effects are significant enough to produce a spectral output with characteristic harmonics, $n$, of the fundamental $n = 1$ having a wavelength, $\lambda_n$, given by,

\[ \lambda_n = \frac{\lambda_u}{2ny^2} \left(1 + \frac{K^2}{2} + \gamma^2 \theta^2 \right) \quad (3.14) \]

The importance of equation (3.14) is that the wavelength emitted is determined by the strength of the magnetic field through the $K$ parameter. When this is possible, the
insertion device is called an undulator. A wavelength may be “selected” by optimizing the magnetic field to produce a band of radiation where the desired wavelength is at peak flux. This is normally accomplished by changing the distance, referred to as the undulator gap, between the opposing magnetic arrays.

Experiments performed in this thesis used a high brightness U100 undulator at the ALS. U100 is approximately 4.3m long with 43 periods, and typically provides a linearly polarized spectral bandwidth of $10^{12}$ photons/sec /mm rad/0.01% BW, and a resolving power ($E/\Delta E$) of 10,000. The energy range is 12-1500eV with a usable spectral range of 16.8-350eV dictated by the monochromator. [105, 106] The energy range, high brightness, and high resolving power make the U100 undulator ideal for the high-resolution photoelectron spectroscopy experiments performed in this thesis.

3.3.3 Beamline

A beamline is an instrument connected to a storage ring designed to deliver a beam of light generated by a bending magnet, or insertion device to a desired location, typically an experimental apparatus, or endstation, with a desired photon energy and bandwidth by using a series of highly reflective mirrors and gratings, slits, windows, and other optics. This section will discuss general features of beamlines as they pertain to Beamline 10.0.1 at the ALS. Figure 3.3 contains a schematic layout of Beamline 10.0.1 at the ALS, which has been described in more detail elsewhere. [27, 107]

Beamline 10.0.1, and the U100 undulator are operated by a beamline server using an in-house computer program operated directly, or via remote connection. To initially produce the desired photon energy, the K parameter is changed by moving the undulator
Figure 3.3 Schematic layout of Beamline 10.0.1 at the Advanced Light Source, Berkeley, CA. [98, 106, 107]

gap. Following the undulator, a horizontal focusing mirror (M1) is used to focus of the beam at the experimental endstation. A vertical condensing mirror (M2) mirrors focuses the light onto a fixed position entrance slit of the spherical grating monochromator (SGM). A typical beamline will use a monochromator with a diffraction grating, and one or two slits to select the desired photon energy and resolution. The SGM consists of three interchangeable spherical grazing-incidence gratings consisting of a 380 line/mm, 925 line/mm, and a 2100 line/mm. The energy ranges for each grating are 16.8-75eV, 40-160eV, and 100-360eV, respectively. The energies can be calculated by equation (3.15).

\[ m\lambda = 2d(\sin\alpha + \cos\beta) \]  \hspace{1cm} (3.15)

Where \( m \) is the diffraction order, \( d \) is the groove spacing, and \( \alpha \) and \( \beta \) are the incident and reflected angles with respect to the grating. The relation between the two is given by

\[ 2\theta = \alpha - \beta = constant, \]  \hspace{1cm} (3.16)
and means equation (3.15) can be expressed as

\[ m\lambda = 2d\sin(\theta)\cos(\beta + \theta). \] (3.17)

The fixed angle, \(2\theta\), is 165° for the SGM at Beamline 10.0.1. The selected grating is rotated to produce the desired photon energy. The spherical gratings must be manually selected, but selecting the desired energy range within the spherical grating is an automated process. A translating exit slit is positioned at the focal point as given by equation (3.18), and refocused by another mirror (M3).

\[ r_2 = \frac{r_1 R \cos^2 \beta}{R \cos^2 \alpha + r_1 \cos \alpha + r_1 \cos \beta} \] (3.18)

\( R \) is the radius of curvature for the grating (21m), and \( r_1 \) is the distance between the fixed slit and the grating (1.45m). The horizontal deflecting mirrors are only used to select the desired endstation, and do not change during the experiment. Spectral resolution, \( \Delta \lambda \), of the beamline is determined by the quadrature sum of the entrance, \( S_1 \), and exit slit, \( S_2 \), contributions. Slit widths are determined in following equations.

\[ S_1 = \Delta \lambda_1 m \frac{r_1}{d \cos \alpha} \] (3.19)

\[ S_2 = \Delta \lambda_2 m \frac{r_2}{d \cos \beta} \] (3.20)

\[ \Delta \lambda = \sqrt{S_1^2 + S_2^2} \] (3.21)

The ability to work at high resolution (\( \leq 50 \) meV) over a broad energy range (17-350 eV) with a high flux (\( 10^{12} \) photons/sec/mm rad/0.01% BW) was critical to the success of the experiments performed in this thesis.
3.4 High-Resolution Photoelectron Spectroscopy

As mentioned earlier, photoelectron spectroscopy is widely used to study the electronic, vibrational, and geometric structure of specific ionic states when electrons are removed from selected molecular orbitals. In my studies, I will be focusing primarily on the ionization process itself. Transitions can be selectively studied based on their binding energy due to the conservation of energy as mentioned beforehand in equation (3.1). Although the photoelectric effect was first discovered in metals by Hertz in 1887 and the ionization of gases by ultraviolet light in 1900 by Lenard. [108], the technique for analyzing electronic structure was not fully developed until the 1960’s. [109-114]

3.4.1 Electron Spectrometer

Beamline 10.0.1 employs a moveable spectrometer chamber. Detailed information about the chamber and spectrometer can be found in references [27] and [115], respectively. To accommodate the higher operating pressure of the chamber, a differential pumping section is used between the chamber and the beamline to maintain ultrahigh vacuum. The interaction region, electron lenses, and analyzer are shielded by mu-metal layers to protect the photoelectrons from stray magnetic fields, such as the earth’s magnetic field. The chamber may be equipped with either a gas cell on the beam axis, or molecular beam assembly to deliver the target to the interaction region. For experiments presented in this work, a gas cell is used to increase sample density by approximately one hundred times the chamber pressure. Typical operating chamber pressure is $10^{-5}$-$10^{-7}$ Torr with a base pressure of $10^{-9}$ Torr.

Photoelectrons are analyzed using a commercial hemispherical electron energy analyzer with a mean radius of a 200 mm (Scienta SES2002). The instrument uses a
multi-element electrostatic lens system to focus and transfer electrons from the interaction region to the entrance slit of the analyzer. The analyzer can be rotated from $\theta=0^\circ$-$90^\circ$ for angular distribution studies, but is positioned at $\theta_m=54.7^\circ$ with respect to the photoionization angle. This is known as magic angle photoelectron spectroscopy as $54.7^\circ$ is the angle at which the photoelectron intensities are independent of detection angle. This eliminates the need to correct for photoelectron asymmetry that is discussed in the following section. The system uses concentric hemispheres and electrostatic steering lenses to separate and guide electrons to the detector. The detector stack consists of two microchannel plates (MCP) and a phosphor screen. Radiation emitted from the screen is collected with a CCD. The pass energy ($E_p$) is the kinetic energy of electrons at the center of the detected energy band while passing through the hemispherical analyzer, and determines the width of the energy range included by the multielement detector. The $E_p$ was 2, 5, 10, or 20eV depending on the excitation energy for each experiment. Exit slit widths were between 0.1 and 4.0mm. The theoretical resolution of the analyzer \cite{115} can be described as

$$\Delta E \approx \frac{SE_p}{2R}$$  \hspace{1cm} (3.22)

with a resolving power of

$$RP = \frac{E_p}{\Delta E} \approx \frac{2R}{s};$$  \hspace{1cm} (3.23)

where R is the analyzer radius (200 mm for a Scienta 2002), s is the slit width, $E_p$ is the pass energy. For example, an $N_2$ spectrum is taken at $h\nu=35eV$ with analyzer set with an $E_p=20eV$, and a slit width of 0.3mm will have a theoretical best resolution of 15meV, and a resolving power of $\sim1300$. 

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3.4.2 Asymmetry Parameters in Photoelectron Spectroscopy

Photoelectron scattering is not uniform with respect to direction, nor are the angular distribution uniform with respect to different electronic levels. \[6\] The recorded photoelectron spectra depend on the angle with respect to the photon beam, and the analyzer. The photoelectron angular distributions for plane-polarized light, i.e. linearly, can be express as

\[ I(\theta) = \frac{\sigma}{4\pi} \left[ 1 + \frac{\beta}{2} (3 \cos^2 \theta - 1) \right], \quad (3.24) \]

where \(\sigma\) is the total cross-section integrated over all angles, \(\beta\) is the anisotropy parameter, and \(\theta\) is the angle between the photon polarization vector and the ejected electron. The angular distribution for atoms and molecules is described by \(\beta\), and can range between \(2 \geq \beta \geq -1\). In most cases, \(\beta\) is positive, and typically close to 2. This variable can be avoided by performing experiments using the magic angle, 54.7º. In this
case, the second-order Legendre polynomial becomes zero and equation (3.24) simplifies to

$$I(\theta) = \frac{\sigma}{4\pi} \quad (3.25)$$

The intensity of a transition is now directly proportional to the total cross-section.

### 3.4.3 Thermal Doppler Broadening and Other Broadening Sources

The main source of resolution loss for synchrotron-based experiments is thermal Doppler broadening. As the kinetic energy of the electron is increased, the Doppler broadening increases, and the thermal motion of the molecule can affect the kinetic energy. This can be explained with a simple derivation. Consider that the molecules are moving isotropically with speed $\nu$. (We will average over the thermal distribution of speeds shortly.) Electrons have a mass, $m$, and a velocity, $\xi$, relative to the target molecule. The electron energy will be at maximum when the electron is ejected in the same direction as the target molecule, and at minimum when ejected in the opposite direction. This can be denoted by equations (3.26).

$$E'_{\text{max}} = \frac{1}{2} m (\nu + \xi)^2 \quad (3.26)$$

$$E'_{\text{min}} = \frac{1}{2} m (\nu - \xi)^2$$

The total broadening can be expressed as

$$\Delta E' = 2mv\xi, \quad (3.27)$$

and the full width at half maximum (FWHM) of the electron energy profile, $\delta$, is equal to half of the total broadening, $\Delta E'/2$. The target molecules have a typical velocity of

$$\nu = (2kT/M)^{1/2} \quad (3.28)$$
corresponding to a Maxwell distribution where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature in K, and \( M \) is the mass of the target molecule. Substituting equation (3.27) into equation, the FWHM is given by

\[
\delta = 2\left(\frac{mE_kT}{M}\right)^{1/2},
\]  
(3.29)

where \( E = \frac{1}{2}mv^2 \). By using atomic mass units for \( M \), and \( E \) is electron kinetic energy in electron volts, equation (3.29) simplifies to

\[
\delta (\text{meV}) = 0.723 (ET/M)^{1/2}.
\]  
(3.30)

Doppler broadening was one of the main sources of loss of resolution particularly at high photon energies, and at high temperatures for the nucleobase experiments. For ICN, the typical vibrational spacing is 7-15 meV. [52] The Doppler broadening at 293 K for \( E_k=10.0 \) eV is 3.1 6meV, and at \( E_k=150 \) eV the broadening is 12.3 meV. A straight forward technique to reduce Doppler broadening is by employing a supersonic molecular beam (SSMB) to reduce the absolute temperature to approximately 15K. The disadvantage of a SSMB is the reduced sample density in the interaction region, and in turn reduced signal that could not be afforded with the limited available beamtime at Beamline 10.0.1.

Natural lifetime broadening and pressure broadening are potential sources for decreased resolution. [7] Due to the nature and design of the experiments, they have little effect on the resolution, and will only be briefly covered. Natural lifetime broadening is expressed as

\[
E(\text{eV}) = \frac{\hbar (\text{eV}\cdot\text{s})}{\tau_{sp}(\text{eV}^2)}.
\]  
(3.31)

where the reduced Planck constant, \( \hbar \), is equal to 6.5x10^{-16}eV\cdot\text{s}, and \( \tau_{sp} \) is the intrinsic lifetime of the transition. According to the Franck-Condon approximation, the lifetime of
an electronic transition is near instantaneous making the natural lifetime broadening negligible. Pressure broadening is expressed as

$$E(\text{eV}) = bph, \quad (3.32)$$

where $b$ is the pressure-broadening coefficient of the target, $p$ is the pressure in the interaction region, and the Plank constant is $4.1 \times 10^{-15} \text{eV} \cdot \text{s}$. For a typical experiment $b = 10^6 \text{Torr/s}$ and $p_{\text{max}} = 10^{-3} \text{Torr}$, the pressure broadening is $4 \times 10^{-12} \text{eV}$.

### 3.5 Data Analysis

The data analysis required for these experiments required only a few steps. First, the kinetic energy of the photoelectron spectra were corrected for errors in the beamline, instrument energy calibration, and as the result of “contact potentials” in the interaction region where ionization occurs using well characterized known spectra, or an internal standard. Next, the individual peaks within each spectrum were fit with Gaussian curves with identical full width at half max (FWHM) for each peak within an electronic level. The peaks were integrated using a software package, Igor Pro™ [117] with the macro, Spectrum Analysis by Curve Fitting (SPANCF). Finally, the vibrational branching ratios were determined by taking the ratios of an individual vibrational intensity with either with the ground vibrational intensity (i.e., $I_v/I_0$) or the sum of vibrational intensities (i.e., $I_v/\Sigma I_v$).
Chapter Four: Chemically-Induced Nonresonant Coupling

4.1 Introduction

Cyanogen halides appeared to be ideal candidates for a study of mode-specific photoelectron scattering over a broad energy range. First, forbidden transitions are well documented in several valence levels. [17, 18, 52, 53, 118] Second, previously published theoretical calculations for the valence levels have indicated the presence of vibronic coupling. [118, 119] For this study, it was possible to probe all of the vibrational degrees of freedom: symmetric stretch, bend, and asymmetric stretch. This permits a “global” view of the correlation between the nuclear and electronic degrees of freedom during photoionization, and how the photoelectron can couple to alternative vibrational modes in polyatomic molecules.

4.2 Background for ICN and BrCN $2\pi^{-1}$

The photoionization spectrum of ICN and BrCN has been studied previously in the 1970’s and 1980’s with partially resolved vibronic structure.[18, 120, 121] The first studies with significantly high resolution (<10meV) were performed by J. Eland et al in the 1990’s with a HeI resonance lamp (hν = 21.2eV), and the assignments of the vibrational substructure for these electronic states have been established with high precision[17, 52]. This is significant for two reasons. First, these studies establish that a resolution of ~10meV is sufficient to resolve the principal vibrational features of the valence levels of ICN and BrCN, and give an indication of the resolution that will be necessary at higher photon energies. Second, the appearance of forbidden bending and asymmetric stretching in the spectra are an indication of non-Franck-Condon behavior,
and raises the possibility that the Franck-Condon breakdown is due to intrachannel effects.

In addition to the high-resolution spectroscopy experiments at a fixed energy, significant work has been performed on CN-containing molecules. Previous studies have established the presence of shape resonances affecting the photoionization dynamics of angular distributions, and branching ratios. [122-126] Holland et al. measured the energy dependence of the photoelectron asymmetry parameter (β), and the electronic branching ratios for of ICN and BrCN 2π\(^{-1}\) photoionization over the energy range 14≤hν≤120 eV. [119] Holland defines an electronic branching ratio as the intensity of an electronic level divided by the sum of the intensity in all the energetically accessible levels. Although spectra were vibrationally unresolved, well-defined variations in the asymmetry parameter were measured. A sharp dip of the asymmetry parameter at hν ≈ 20eV was recorded for BrCN 2π\(^{-1}\). The dip was assigned as a 2π→kσ shape resonance. Several broad variations were observed in the ICN 2π\(^{-1}\) asymmetry parameter as well as in the electronic branching ratio.

Figure 4.1 Electronic branching ratio for ICN\(^+\)(X^2\Pi) by Holland et al. [119]
The $2\pi \rightarrow k\sigma$ deviations were considered to a result of multiple resonant and non-resonant processes. A Mulliken population analysis was performed for ICN $2\pi^1$ and BrCN $2\pi^1$. The results indicate that the iodine on ICN can be treated as an atomic-like system, but not for bromine on BrCN. A continuum multiple scattering (CMS-$X\alpha$) approach was used to identify the origins of the excursions in the electronic branching ratios and asymmetry parameters. The $k\sigma^+$ ($h\nu=21$ eV) and $k\pi$ ($h\nu=14$ eV) resonances were a result of centrifugal barrier trapping of $l=3$ waves on iodine. The nonresonant feature at $h\nu=73$ eV was attributed to Cooper minima of the $l=2$ and 3 partial waves. The feature of $h\nu=60$ eV corresponds to an intershell coupling with the 4d channel.

The main result that will follow is that we have observed wide-ranging Franck-Condon breakdown, and that a novel mechanism is responsible. In fact, our experimental observations led to theoretical work by Lucchese, which ultimately has elucidated the underlying mechanism. The combination of our experimental and his theoretical work helped clarify the origin of the forbidden transitions, and the dependence of their intensities on the excitation energy. Previous studies have elucidated that normally forbidden transitions become allowable because of instantaneous symmetry breaking. [20, 23, 24, 49-51, 80] Intrachannel coupling, first suggested by Herzberg [1], occurs when the inclusion of the vibrational wavefunction in the molecular dipole matrix elements as described in Chapter 2 produces to a non-zero dipole matrix. By not invoking the Franck-Condon approximation in eq. 2.24, the electronic transition dipole moment is not factored from the vibrational integral, which allows for a single quantum excitation of non-totally symmetric vibrations to occur; this requires some mechanism that causes the electronic matrix elements to vary with changes to the molecular geometry. [20, 23, 24,
Numerical calculations based on the Schwinger variational method are presented to support these notions. The calculations were performed using single-channel frozen-core Hartree-Fock approximation (SCFCHF) by our collaborator, Robert Lucchese of Texas A&M University. Experimental and the theoretical results will be discussed in the following sections.

4.3 Photoionization Results

4.3.1 Cyanogen Iodide $2\pi^\dagger$

4.3.1.1 Photoelectron Spectra

Figure 4.2 contains the outer valence shell photoelectron spectrum of ICN. The valence shell molecular orbital configuration of the cyanogen halides in their electronic ground state is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(2\pi)^4$. The adiabatic binding energy for each orbital is $10.903\text{ eV (}\Omega=3/2)$, $11.443\text{ eV (}\Omega=1/2)$, $13.163\text{ eV}$, $13.39\text{ 4eV (}\Omega=3/2)$, and $13.562\text{ eV (}\Omega=1/2)$, respectively. [18, 52] Our results were consistent with the spacing for these values, and our spectra were shifted to agree with the ground state ionization potential.

Figure 4.3 contains the section of the photoelectron spectrum containing the ICN$^+X^2\Pi$ state with the $\Omega=3/2$ and $\Omega=1/2$ spin-orbit components. This spectrum was taken with an excitation energy of $h\nu=20\text{eV}$, which is close to the previously used energy of HeI at $h\nu=21.2\text{ eV}$. The spectrum contains twelve features with significant intensity, of which the five-labeled peaks are well resolved from neighboring vibrations. They are the ground state ($v^+=000$, $E_b=10.903\text{eV and }11.440\text{eV}$), the asymmetric stretching mode ($v^+=001$, $E_b=10.969\text{ eV and }11.508$), the symmetric stretching mode ($v^+=100$,
Figure 4.2 Overview of the photoelectron spectrum of ICN at $h\nu=20$eV.

Figure 4.3 The photoelectron spectrum of ICN$^+$(X$^2\Pi$). The most intense vibrations of the $\Omega=3/2$ and $\Omega=1/2$ spin-orbit components are labeled.
Table 4.1 Peaks in the photoelectron spectrum of ICN$^+$($X^2\Pi$).

<table>
<thead>
<tr>
<th>ICN$^+$($X^2\Pi$)</th>
<th>$\Omega=3/2$</th>
<th>$\Omega=1/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
<td>Energy (eV)</td>
<td>Energy (eV)</td>
</tr>
<tr>
<td>010-011</td>
<td>10.834</td>
<td>11.373</td>
</tr>
<tr>
<td>000-001</td>
<td>10.842</td>
<td>11.379</td>
</tr>
<tr>
<td>020-020</td>
<td>10.886</td>
<td></td>
</tr>
<tr>
<td>010-010</td>
<td>10.896</td>
<td>11.434</td>
</tr>
<tr>
<td>000</td>
<td>10.9042</td>
<td>11.441</td>
</tr>
<tr>
<td>010</td>
<td></td>
<td>11.469</td>
</tr>
<tr>
<td>040-020</td>
<td>10.94</td>
<td>11.483</td>
</tr>
<tr>
<td>030-010</td>
<td>10.95</td>
<td>11.493</td>
</tr>
<tr>
<td>020</td>
<td>10.96</td>
<td>11.501</td>
</tr>
<tr>
<td>001</td>
<td>10.969</td>
<td>11.508</td>
</tr>
<tr>
<td>040</td>
<td>11.1014</td>
<td>11.56</td>
</tr>
<tr>
<td>021</td>
<td>11.027</td>
<td>11.569</td>
</tr>
<tr>
<td>002</td>
<td>11.039</td>
<td>11.578</td>
</tr>
<tr>
<td>110-010</td>
<td>11.1434</td>
<td>11.674</td>
</tr>
<tr>
<td>100</td>
<td>11.154</td>
<td>11.68</td>
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<td>120</td>
<td>11.209</td>
<td>11.741</td>
</tr>
<tr>
<td>101</td>
<td>11.219</td>
<td>11.749</td>
</tr>
<tr>
<td>200</td>
<td>11.401</td>
<td>11.916</td>
</tr>
</tbody>
</table>

$E_b=11.154$ eV and 11.680 eV), and two quanta excitation of the symmetric bend ($v^+=200$, $E_b=11.916$ eV) for their respective spin-orbit. Table 4.1 lists vibration and binding energy of all 34 vibrations including remaining 29 vibrations that we did not investigate, either because of weak intensity or insufficient resolution.

Direct integration of the vibrational modes was not possible, so peaks were fitted with Gaussian functions in the commercially available software program Igor Pro™. [117] Gaussian curves were placed at the center of the binding energy given by Eland et al [52], and the FWHM were held constant within each spectrum. The peaks were next fitted for intensity, and integrated for the area. The integrated areas of the peaks were
used to calculate the vibrational branching ratios. Figure 4.2 Overview of the photoelectron spectrum of ICN at $h\nu=20\text{eV}$.

4.3.1.2 Vibrational Branching Ratio Curves

To understand the mechanism that results in the forbidden transitions in the ICN $2\pi^1$ photoionization, we must measure the vibrational branching ratios over a relatively broad energy range, and at relatively small increments. Beamline 10.0.1 has an energy range of $17\leq h\nu\leq 350\text{ eV}$, and ICN$^+(X^2\Pi)$ state has an ionization energy of 10.903 eV. Therefore, the near-threshold shape resonance for cyanogen containing molecules covered in the literature, [119, 123, 125, 126] and by our collaborators’ theoretical treatment was not covered. The ICN $2\pi^1$ photoionization was studied over the photon energy range of $20\leq h\nu \leq 160\text{ eV}$ in $\leq 5\text{ eV}$ steps. The maximum energy range was limited due to availability of beamtime, and the decreasing photoionization cross-section.

![Vibrational Branching Ratio Curves](image)

Figure 4.4 Vibrational branching ratios for symmetric and asymmetric stretching motion of ICN$^+(X^2\Pi)$. Note the broad-ranging (i.e., nonresonant) Franck-Condon breakdown; which is the result of an initial state charge transfer.
The ICN$^+$(X$^2\Pi$) state vibrational branching ratios are given in figure 4.4. The left frame contains the experimental branching ratios of the $v^+=(001)/v^+=(000)$ for the $\Omega=3/2$ and $\Omega=1/2$ spin-orbit components. The right frame contains the experimental branching ratios of the $v^+=(100)/v^+(000)$ for the $\Omega=3/2$ and $\Omega=1/2$ spin-orbit components. Theoretical calculations were performed by Lucchese to determine the origin of these features.

4.3.2 Cyanogen Bromide 2π⁻¹

4.3.2.1 Photoelectron Spectra

Figure 4.5 contains the outer valence shell photoelectron spectrum of BrCN. The valence shell molecular orbital configuration is identical to that of all cyanogen halides as mentioned earlier in section 4.3.1.1. The adiabatic binding energy for the three outer most orbitals is 11.862 eV, 13.56 eV, and 14.188 eV respectively. [17] Our results were consistent with the spacings and the spectra were shifted to correspond to the ground state ionization potential.

Figure 4.6 contains the section of the photoelectron spectrum containing the BrCN$^+(X^2\Pi)$ state with the $\Omega=3/2$ and $\Omega=1/2$ spin-orbit components. This spectrum was collected at excitation energy of $h\nu=20$eV. The spectrum contains 42 vibrations and 3 hot bands. Seven vibrations have been marked for comparison with ICN$^+(X^2\Pi)$. They are the ground vibrational state ($v^+=000$, $E_b=11.860$ eV and 12.044 eV), the asymmetric stretching mode ($v^+=001$, $E_b=11.940$ eV and 12.125 eV), the symmetric stretching mode ($v^+=100$, $E_b=12.096$ eV and 12.279 eV), and two quanta excitation of the bend ($v^+=200$, $E_b=12.508$ eV). As with cyanogen iodide, the remaining features were either of weak
Figure 4.5 Overview of the photoelectron spectrum of BrCN at $h\nu=20$ eV.

Figure 4.6 The photoelectron spectrum of BrCN$^+(X^2\Pi)$ state. The predominant vibrations of the $\Omega=3/2$ and $\Omega=1/2$ spin-orbit components are labeled.
intensity, or of insufficiently resolved to be studied. The integrated areas of the peaks were determined as described in the previous section for cyanogen iodide. Gaussian curves were placed at the center of the binding energy given by Eland et al. [17]

Table 4.2 Peaks in the photoelectron spectrum of BrCN\(^+\)(X\(^2\)\(\Pi\)).

<table>
<thead>
<tr>
<th>BrCN(^+)(X(^2)(\Pi))</th>
<th>(\Omega=3/2)</th>
<th>(\Omega=1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
<td>Energy (eV)</td>
<td>Energy (eV)</td>
</tr>
<tr>
<td>000</td>
<td>11.8602</td>
<td>12.0443</td>
</tr>
<tr>
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</tr>
<tr>
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<td>12.1179</td>
</tr>
<tr>
<td>001</td>
<td>11.94</td>
<td>12.125</td>
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<td>12.0044</td>
<td>12.198</td>
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<td>12.3692</td>
</tr>
<tr>
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</tr>
<tr>
<td>300</td>
<td>12.5583</td>
<td>12.7335</td>
</tr>
</tbody>
</table>

4.3.2.2 Vibrational Branching Ratio Curves

Figure 4.7 contains the vibrational branching ratios for BrCN 2\(\pi^1\). The top frames contain the experimental branching ratios of the \(v^+\=(001)/v^+\=(000)\), and the bottom flames include the \(v^+\=(100)/v^+\=(000)\) for the \(\Omega=1/2\), and \(\Omega=3/2\) spin-orbit components. The minimum photon energy of Beamline 10.0.1 is 17eV, which is above the ground excited state ionization energy of cyanogen bromide at 11.860eV. Therefore, the near-threshold shape resonance for cyanogen-containing molecules was not completely
Figure 4.7 Vibrational branching ratios for BrCN\(^+\)X\(^2\Pi\) with a near threshold shape resonances. While the data points were taken at 1eV steps, they were averaged to cleanup the figure, and do not affect the results.

covered experimentally. [119, 123, 125, 126] The BrCN \(2\pi^{-1}\) photoionization for studied over the photon energy range of 20 to 120 eV at 1eV steps over the resonant feature and 5eV steps over the rest. The energy range displayed, \(20 \leq h\nu \leq 80\) eV, is to emphasize the
resonant feature near threshold, as the higher energy branching ratio becomes level. Theoretical calculations were performed to confirm the source of the resonant energy dependence over the energy range studied as the result of a shape resonance.

4.4 Discussion

The photoionization dynamics for ICN $2\pi^{-1}$ has only been briefly examined over a similar energy range as the current study, and only for vibrationally unresolved electronic states by Holland et al. [119, 123, 125, 126], as discussed earlier. While they reported the non-Franck-Condon behavior in the electronic branching ratios as the result of an intershell coupling at $h\nu=60$ eV, a Cooper minimum at $h\nu=73$ eV, and no features above $h\nu=100$ eV. [119] Our vibrational branching ratios do not agree with their results, and warranted a theoretical examination of the discrepancy.

In order to understand the source of the nonresonant phenomena observed in the experimental vibrational branching, theoretical calculations were performed by Prof. Robert Lucchese as mentioned earlier. His work involves calculating the continuum electron wavefunction using Hartree-Fock level wavefunctions, and the accompanying dipole matrix elements that define the partial photoionization cross-section. Vibrational motions were treated as adiabatic in accordance with the Born-Oppenheimer approximation, so interchannel effects such as Herzberg-Teller coupling were not included. His calculations did not invoke the Franck-Condon approximation, so any effects that he predicts occur within the Born-Oppenheimer framework, but do not depend on the validity of the Franck-Condon approximation. A comparison of experimental and theoretical results is displayed in figure 4.8; which confirm the presence of broad range non-resonant phenomena for the $v^+=(100)/v^+=(000)$, and the
$v^+ = (001)/v^+ = (000)$ curves. It is important to note that vibrational mode $v_1$ corresponds principally to the C-N vibration, while mode $v_3$ corresponds a primarily I-CN stretch.

Figure 4.8 shows a very strong and extended dependence of the $v^+ = (100)/v^+ = (000)$ branching ratio on energy, so it is useful to ask what is happening for this vibration. Recall that this vibration is primarily a stretch between the C and N atoms.

![Graph showing vibrational branching ratios](image)

waves as the $q_1$ normal coordinate is varied.

Figure 4.8 Comparison of the experimental and Schwinger variational calculations for the ICN$^+ (X^2\Pi)$ vibrational branching ratios. Calculations were performed for the $v^+ = (100)/v^+ = (000), v^+ = (001)/v^+ = (000)$ branching ratios for the $\Omega = 3/2$ and $\Omega = 1/2$ spin-orbit over the energy range $20 \leq \hbar \nu (eV) < 170$. The theoretical results shown above express how large partial waves behave as the I-CN distance is varied, as discussed below.

Figure 4.8 contains the theoretical plot of the contributions from selected higher partial waves as shown in figure 4.9. A detailed analysis reveals that the high partial waves, particularly the $l=14\partial$, arise primarily from the ejection of electrons from the I-atom. The interesting point is that the theoretical calculations demonstrate that there is a charge
transfer process that takes place as the CN bond is stretched, whereby electron density is transferred from the CN moiety to the I-atom. Thus, our combined experimental/theoretical effort (due to Lucchese) demonstrates that the initial (target) state is changing as the molecule undergoes a vibration along the $q_1$ coordinate, and that the transfer of electron density to the I-atom accentuates these high partial wave components. Thus, the molecule undergoes ionization more strongly in this spectral region centered around 100 eV *when the molecule is excited in the $v_1$ mode*. This is another way of saying that the electronic transition dipole moment depends strongly on vibration. However, this effect is not the result of the photoelectron dynamics like the other examples that have been described in chapter 2, such as shape resonances or Cooper minima induced effects; in those instances, it is the continuum electron that is responding to changes in molecular geometry. In the case of ICN, the non-Franck-Condon behavior arises because the target wavefunction itself is strongly geometry-dependent. The non-Franck-Condon effect is the product of a charge transfer between the I-atom and the CN moiety resulting in geometry-dependent electronic structure changes in the initial state wavefunction. I refer to this novel mechanism as a *chemically-induced nonresonant coupling: a charge-transfer effect in the initial state*.

A simple analysis indicates that the initial state sensitivity to geometry should be present for the other cyanogen halides. To further understand the source of the chemically-induced, charge transfer Franck-Condon breakdown observed for ICN $2\pi^1$, the project turned to valence isoelectronic systems, i.e. BrCN. To see this, we estimate the sensitivity of the initial electronic state to changes in the geometry was estimated by
Figure 4.9 Plots of specific partial wave contributions for different values of the \(q_1\) normal coordinate (this is dominated by the C–N distance).

Figure 4.10 Mulliken population of the CN part of the HOMO in the XCN molecules. In all three cases the equilibrium geometry has \(R(\text{CN}) = 1.16\ \text{Å} \)
examining changes in the Mulliken populations of the $2\pi^{-1}$ orbital. In figure 4.10, the Mulliken populations of the HOMO on the CN fragment as a function of the CN bond length for ClCN, BrCN, and ICN has been plotted. The HOMO is a $\pi$ orbital that is a linear combination of a lone pair $\rho$ orbital on the halogen and the bonding $\pi$ orbital on the CN moiety. The trend indicated here is the result of the $\pi$ orbital on CN being pushed to higher energy as the CN bond length increases. This then increases the amount of the CN $\pi$ orbital in the HOMO. This initial state geometry effect is the source of the non-Franck-Condon behavior in ICN.

4.5 Summary of the ICN and BrCN $2\pi^{-1}$ Results

In summary, the discovery of a novel class of non-Franck-Condon behavior presents a new direction in the topic of photoionization dynamics. The origin of the geometry-dependent electronic structure changes in the initial state wavefunction has been evaluated by a collaboration of experimental and theoretical tools. The data shows the initial state geometry effect is fairly sensitive to bond length. The deviation from Franck-Condon behavior may not occur without a sufficient Mulliken population. The results demonstrate the necessity of vibrationally resolved studies of polyatomic molecules over a broad energy range is essential in understanding the processes in the photoionization scattering dynamics.
Chapter Five: Vibrationally Resolved Spectra and Their Energy-Dependent Behavior for Asymmetric Polyatomic Systems: Nucleobases

5.1 Introduction

To date, photoionization dynamics studies performed at the vibrationally resolved level of detail have consisted primarily of simple diatomic, triatomic, and highly symmetric systems. [20, 21, 26, 77, 131-136] As a natural progression, it is of interest to focus on larger, more complex polyatomic systems. With the recent growth of research into biological systems, DNA/RNA bases and their related compounds are a logical next step, as they represent a new class of systems, and it is likely that new resonant and nonresonant photoionization features will emerge.

We have chosen nucleic acid bases specifically for this study for a few reasons. First, probing how continuum electrons in a photoionization process interact with a DNA/RNA molecule can be very useful in understanding how low energy electrons scatter from DNA/RNA molecules in electron scattering processes. Moreover, the photoionization measurements have the additional benefit that vibrationally resolved data can be generated, which is typically not true for the electron scattering studies. It may be possible to generate new insights into how low energy electrons result in DNA damage as a result of photoelectron trapping dynamics that are expected to occur [137, 138] and are related to strand breaking phenomena observed in electron impact studies. [139-148] Secondly, the desired vibrationally resolved photoelectron spectra are likely to be feasible, given that the molecular frames are relatively rigid, and there not large numbers of conformers that might complicate the analysis. The technical challenge of producing a vibrationally resolved photoelectron spectra of gas phase nucleobases alone is of significant interest. [149-151]
At the outset, we note that the work reported here has not investigated the dependence of the vibrational structure on the incident photon energy. The purpose of this work is simply to see whether vibrationally resolved data are even feasible for a traditional photoelectron spectroscopy measurement. The typical attainable resolution of the Scienta SES 2002 analyzer is on the order of a few meV. Due to the low vapor pressure of biological materials, samples were slowly heated with an in-vacuum oven to produce sufficient sample density in the interaction region. As the temperature was typically between 200°C and 400°C for each sample, thermal Doppler broadening, and sample decomposition quickly becomes a concern.

Give the initial encouraging results from this study; future investigations will examine the incident photon energy dependence of the relatively vibrational intensities. Future studies by my research group will search for evidence of both resonant and nonresonant mechanisms that couple photoelectron motion with molecular vibration, and stimulate collaborative studies with theorists wishing to develop state-of-the-art potential energy surfaces of these systems.

5.2 Background

Experimentalists and theorists have been attempting to obtain highly resolved photoelectron spectra of nucleobases, and to assign orbitals to the features in their electron spectra since the 1970’s. [152-170] The most recent experimental and theoretical studies were performed by Trofimov et al in 2006 and Holland et al in 2008. [11, 171] They combined many-bodied Green’s functional method (ADC(3)) with angle-resolved photoelectron spectra to measure the asymmetry parameter to determine the electronic configuration of the outer orbitals of several nucleobases. They achieved a resolution of
approximately 50-100meV at the Daresbury Laboratory, UK synchrotron using a hemispherical analyzer and a two-stage oven, but were still unable to obtain vibrational resolution. These studies were able to assign the photoelectron bands with some certainty, established the minimum vibrational width must be <50meV, and provided the basis for a stable gas-phase sample delivery method.

5.3 Experimental and Analysis

As stated in the introduction, nucleobases have an extremely low vapor pressure (<10^{-11} Torr), which required ample heating to produce sufficient sample density in the interaction region. Target samples were vaporized by using a two-stage resistively heated, aluminum oven under vacuum as seen in figure 5.1. Stage one was designed with a removable sample cup for quick sample change out during an experimental run, and an external feed though for a calibration gas. A cartridge heater capable of temperatures in excess of 500ºC was installed in the base of the oven. Stage two consisted of a transfer tube to deliver the sample in side the mu-metal shielding, and was kept 10-20ºC above the temperature of the line to minimize sample deposition. The samples were heated at ~10ºC/min to reduce sample decomposition.

Due to the complex nature of the DNA base spectra as a result of their complex structure, potential isomers, and hotbands; no direct method can be used to identify and fit complex vibrational structure of nucleobases. While not a perfect tool to fit spectra, the following method describes how fitting curves were assigned to illustrate the complexity of the nucleobase spectra later on in this chapter. For each electronic level in the spectrum, the most predominate peak was selected to be fit for intensity and FWHM in Igor Pro™. [117] Additional peaks were manually inserted into the program
Figure 5.1 The two-stage resistively heated, aluminum oven used to vaporize the nucleobases samples. Typical operating temperatures were 200-400°C.

fit using the same FWHM. The SPANCF macro mentioned early automated the movement of peaks in energy (y-axis) and intensity (x-axis) to reduce the $\chi^2$ value measured by the program. Periodically the FWHM of the predominate peak would be reevaluated keeping the intensity constant, and the FWHM of the other peaks in the electronic level would be changed to match. The correctness of the fit was tested in two ways. The first involved adding random additional peaks to the fit. The SPANCF macro would then attempt to fit the peak to the spectrum. The result would be the intensity of the peak going to zero, or the reduction of the intensity of all peaks. The second test involved removing random peaks and allowing the program to refit the spectrum. If too many peaks were used, the peaks would space out and increase in intensity keeping the $\chi^2$ at the same value. If too few, the $\chi^2$ would worsen when the peaks attempted to fit the data. We are well aware that the fitting procedures used are not necessarily physically
meaningful, but they represent a starting point for additional analysis. A complete list of vibrational energies, intensities, and FWHM for each nucleobase fit can be found in Appendix A.

5.3.1 Photoionization Results

5.3.1.1 Uracil

Figure 5.2 shows four outer most valence shells for the photoelectron spectrum of uracil at $h\nu=60$eV. The outer valence configuration is $(11a'(\sigma))^2$ $(1a''(\pi))^2$ $(12a'(\sigma))^2$ $(13a'(\sigma))^2$ $(14a'(\sigma))^2$ $(2a''(\pi))^2$ $(3a''(\pi))^2$ $(15a'(\sigma_{O,LP}))^2$ $(16a'(\sigma_{O,LP}))^2$ $(4a''(\pi))^2$ $(5a''(\pi))^2$.

[11] The binding energy ranges are 9.25 to 9.82, 9.82 to 12.43, and 12.43 to 13.22eV respectively for the three regions, which are consistent with previous experimental studies. [11, 154, 155, 170]

Figure 5.2 Overview of the photoelectron spectrum of uracil. The top frame contains experimental data taken at $h\nu=60$eV using magic angle photoionization, $\theta=54.7^\circ$. The bottom frame by Holland et al. [11] was taken at $h\nu=60$eV and $\theta=0^\circ$. 

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Figure 5.3 The photoelectron spectrum of uracil with vibrations fit the first four valence orbitals at $h\nu=60\text{eV}$.

Figure 5.3 contains the fit photoelectron spectrum consisting of the first four valence orbitals of uracil at $h\nu=60\text{eV}$. The first region consists of the $5a'(\pi)$ orbital, and is comprised of 17 vibrations with a width of 41meV. The second region encompasses two valence levels, $4a''(\pi)$ and $16a'(\sigma_{OLP})$, containing 49 vibrations with a width of 55meV. The third region, $15a'(\sigma_{OLP})$, has 16 vibrations at 55meV.

5.3.1.2 Cytosine

Figure 5.4 shows four outer most valence shells for the photoelectron spectrum of cytosine at $h\nu=60\text{eV}$. Because the sample had to be heated to produce sufficient vapor, cytosine has four potential tautomer/conformer forms producing small variations in the outer valence configuration. [171] For the purpose of study, the tautomer/conformation in figure 5.3 will be used to assign the valence configuration of $(6a(\sigma))^2 (7a(\sigma))^2 (8a(\sigma))^2 (9a(\sigma))^2 (10a(\sigma))^2 (11a(\sigma))^2 (12a(\pi_1))^2 (13a(\sigma))^2 (14a(\sigma))^2 (15a(\sigma))^2 (16a(\pi_2))^2 (17a(\pi_3))^2$
Figure 5.4 Overview of the photoelectron spectrum of cytosine. The top frame contains experimental data taken at $h\nu=50$ eV using magic angle photoionization, $\theta=54.7^\circ$. The bottom frame by Trofimov et al. [171] was taken at $h\nu=80$ eV and $\theta=0^\circ$.

Figure 5.5 The photoelectron spectrum of cytosine with vibrations fit the first four valence orbitals at $h\nu=60$ eV.
according to the ADC(3) calculations performed by Trofimov. \[171\] The binding energy ranges are 7.90 to 9.08, and 9.08 to 10.80 eV respectively for the two regions, and are consistent with previous studies.\[161, 167, 171\]

Figure 5.5 contains the fitted photoelectron spectrum consisting of the first four valence orbitals of cytosine at $h\nu=60$ eV. The first region consists of the $21a(\pi_5)$ orbital, and consists of 8 vibrations with a width of 156 meV. The second region encompasses three orbitals, $18a(\sigma_{O\text{ LP}})$, $19a(\sigma_{N\text{ LP}})$, and $20a(\pi_4)$, containing 21 vibrations with a width of 85 meV.

### 5.3.1.3 Thymine

The four outer valence orbitals of thymine at $h\nu=30$ eV are presented in figure 5.6. Unlike cytosine, thymine has only a cis/trans conformation on the methyl group which can produce a 0.3 eV shift in binding energy of the $15a'(\sigma)$ orbital.\[171\] Previous studies have determined the cis conformation, where the in-plane hydrogen is opposite the C-O double bond, is the most stable, \[172\] and will be used as a basis for assigning the electronic structure for this section (although both isomers could be present, in principle). The cis-thymine valence configuration is $15a'(\sigma)^2 (3a''(\pi_3))^2 (16a'(\sigma))^2 (4a''(\pi_4))^2 (17a'(\sigma_{O\text{ LP}}))^2 (18a'(\sigma_{O\text{ LP}}))^2 (5a''(\pi_3))^2 (6a''(\pi_6))^2$. \[171\] The binding energy ranges are 8.70 to 9.70, 9.70 to 10.86, and 10.86 to 11.7 eV respectively for the three regions, and are consistent with theoretical and experimental values. \[154, 167, 171, 172\]
Figure 5.6 Overview of the photoelectron spectrum of thymine. The top frame contains experimental data taken at $h\nu=30$ eV using magic angle photoionization, $\theta=54.7^\circ$. The bottom frame by Trofimov et al [171] was taken at $h\nu=40$ eV and $\theta=0^\circ$.

Figure 5.7 The photoelectron spectrum of thymine with vibrations fit of the first four valence orbitals at $h\nu=30$ eV.
Figure 5.7 contains the fit photoelectron spectrum consisting of the first four valence orbitals of thymine at hv=30 eV. The first region consists of the 6a"(π₆) orbital, and is contains 20 vibrations with a width of 45 meV. The second region encompasses two orbitals, 18a'(σ_{O LP}) and (5a"(π₅), containing 27 vibrations with a width of 45 meV. The last region, 17a'(σ_{O LP}), has 9 vibrations at 100 meV widths.

5.3.1.4 Adenine

Figure 5.8 shows 5 outer most valence shells for the photoelectron spectrum of cytosine at hv=21.2 eV. Adenine has no other conformer, or tautomer configurations. The outer valence configuration is

\[ (13a(\sigma))^2 (14a(\pi_1))^2 (15a(\sigma))^2 (16a(\sigma))^2 (17a(\sigma))^2 (18a(\pi_2))^2 (19a(\pi_3))^2 (20a(\sigma_{N LP}))^2 (21a(\sigma_{N LP}))^2 (22a(\pi_4))^2 (23a(\sigma_{N LP}))^2 (24a(\pi_5))^2 (25a(\pi_6))^2 \]

[171] The binding energy ranges are 8.00 to 8.90, 8.90 to 9.80, and 9.8 to
11.00 eV respectively for the three regions, and are consistent with previous studies.

[149, 156, 163, 167, 169, 171]

Figure 5.9 contains the fitted photoelectron spectrum of adenine (hv=21.2 eV); it consists of three regions, which contain electronic states formed from ejection of electrons from the five outmost valence orbitals. The first region is the 25a(π₆) composed of 16 vibrations with a width of 60 meV. The second region covers two levels, 23a(σ_{N,LP}) 24a(π₅), containing 17 vibrations with a width of 83 meV. The last region, 21a(σ_{N,LP}) 22a(π₄), has 15 vibrations at 81 meV.

![Photoelectron spectrum of adenine](image)

Figure 5.9 The photoelectron spectrum of adenine with vibrations fit of the first five valence orbitals at hv=21.2 eV.

**5.3.1.5 Guanine**

Figure 5.10 shows four outermost valence shells for the photoelectron spectrum of guanine at hv=21.2 eV. [158] Due to guanine decomposing when heated above 200°C,
and heating required to achieve a minimum sample density in the interaction region, the generated spectra contained many impurity bands, and were not reproducible. The spectrum presented in figure 5.10 is a composite of dozens of spectra with the impurities manually subtracted. The figure is only included for completeness of the nucleobases study.

![Figure 5.10](Image)

Figure 5.10 Overview of the photoelectron spectrum of adenine. The top frame contains experimental data taken at $h\nu=21.2$ eV using magic angle photoionization, $\theta=54.7^\circ$. The bottom frame by Dougherty et al [158] was taken at $h\nu=21.2$ eV.

### 5.4 Discussion

Previous studies on gas phase DNA bases, particularly uracil, cytosine, and thymine, have primarily been concerned with identification of the electronic structure. [11, 90, 91, 154-163, 165-170, 172-176] This is the first study to focus on, and achieve even partially resolved vibrational structure in the gas-phase photoelectron spectra of DNA and RNA bases. It establishes that vibrational resolution is possible laying the foundation for future experimental, and theoretical studies to develop the understanding of fundamental molecular physics as it applies towards larger, asymmetric systems.
Chapter Six: Photoionization Dynamics in Diatomic Molecules

6.1 Introduction

Diatomic molecules are ideal test candidates for examining resonant and nonresonant effects because of their simplicity. Thus, it is possible to obtain a “global” view of the correlation between the nuclear and electronic degrees of freedom during photoionization. In this context, global refers to having a wide-ranging view, and being able to study all the available vibrations, of which there is one. By using state-of-the-art photoelectron spectroscopy techniques, previously unattainable and irresolvable molecular systems and electronic states are accessible for analysis. For example, until recently, the only possible way to obtain highly resolved photoionization data far above threshold was to use dispersed fluorescence. [78, 79, 177, 178] However, such measurements cannot be applied to electronic ground states, which do not fluoresce.

Previous studies have shown that the photoelectron dynamics can be coupled to subtle geometric changes producing profound effects on the photoionization process. [179] The basis for the geometry dependence for Cooper minima is not nearly as well understood as it is for resonant effects. By studying diatomic systems in order to highlight the systematics of such effects, a foundation of knowledge may be built for nonresonant effects in the same way have been done for the resonant processes. The chapter will present the photoionization results of four diatomic systems, N₂, CO, NO, and O₂, covering several electronic states over broad ranges of energy in order to interrogate several fundamental questions of photoionization dynamics. Why are Cooper minima appearing in these molecules in the first place? Why is there a R-dependence on Cooper minima? Why do the isoelectronic systems N₂ and CO behave in an opposite manner?
And why do NO and O$_2$ have only subtle non-Franck-Condon behavior compared to N$_2$ and CO?

6.2 Background

The photoelectron spectra for N$_2$, CO, NO, and O$_2$ have been previously studied, and have had the electronic structure identified for the valence orbitals. [6, 47, 88, 180-182] As apposed to the triatomic systems in chapter 4, only one vibrational mode occurs in diatomics, which greatly simplifies the assignment of the vibrational modes in a spectrum.

The effect of Cooper minima in atomic systems arising from a cancellation effect that occurs in the radial matrix element owing to a radial node have been studied for decades [42, 69, 73, 75, 183-186] The fact that the vibrational motion could couple rather strongly to photoelectron motion by a non-resonant mechanism, i.e. a Cooper minima, over such a broad energy range was quite a revelation. [12, 78, 79, 178] Experiments and theory have shown that Cooper minima can lead to photoelectron vibrational coupling that occurs over huge energy ranges, [12, 79, 179, 187] i.e., more than 10 times the binding energy. However, it is not known if the Cooper minima in the molecules studied arise from atomic nodes, or molecular nodes, or some other mechanism.

CO and N$_2$ valence photoionization has been studied theoretically and experimentally using several techniques, [31, 49, 78, 79, 129, 187, 188] though it was important to note that the work I am reporting here is the first case where the vibrationally resolved behavior has been measured over wide ranges for several electronic states. The first investigation to study the photoionization dynamics using synchrotron radiation to cover a relatively wide spectral range continuously, albeit
without vibrational resolution, was performed Plummer et al. [188] They measured electronic branching ratios of the outer valence levels over the photon energy range 18 to 50 eV. Poliakoff [187], Rao [12, 178], and Farquar [177] used dispersed fluorescence spectroscopy to study the rotational populations and vibrational branching ratios from near threshold to over 125eV above the ionization for the case of N$_2$ 2σ$_u^{-1}$, but were unable to examine the ground state with this technique. The source of the N$_2^+$(B$^2\Sigma_u^+$) deviation has previously been established by fluorescence studies as a result of a bond length dependence of a Cooper minima in the l=2 and l=4 partial waves, [12, 78, 79, 178, 179, 187] while the ground ionic state has been previously unavailable for examination.

While it is of considerable interest to study nonresonant photoelectron-vibrational coupling, it is useful to gain context by comparing the results to resonant effects such as shape resonances. The example of shape resonances is particularly relevant in that the spectral extent of their effects is normally considered to be relatively broad. For example, the well-known 3σ$_g$ → kσ$_u$ in N$_2$ is usually considered to be extremely wide-ranging, as its effects on vibrational branching ratios and photoelectron asymmetry parameters extend over 10-15 eV. This example is mentioned to place our recent results on N$_2$ and CO into context. In addition to the N$_2$ and CO studies, we have also acquired extensive data sets for NO and O$_2$. Note that there are many electronic states that are accessed, which is a consequence of starting with an open-shell configuration. The O$_2$ photoelectron spectrum is similar in this regard, and has theoretical studies predicting R-dependent shape resonances for several vibrational branching ratios. [61, 62]
6.3 Photoionization Results

6.3.1 An Isoelectronic Comparison: N$_2$ and CO

6.3.1.1 Photoelectron Spectra

Figure 6.1 contains the valence shell photoelectron spectrum of N$_2$. The molecular orbital configuration for nitrogen is $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4 (3\sigma_g)^2$. The adiabatic binding energy for each orbital is 15.576, 16.693, 18.757, and 23.583 eV respectively. [44, 88, 182, 189] Our results were consistent with these results, and our spectra were shifted to agree with the ground state ionization potentials. Because of the simplicity of the vibrational structure for most electronic levels, a detailed view will not be given unless warranted by the overlap of multiple levels.

![N$_2$ photoelectron spectrum at hv=40 eV](image)

Figure 6.1 Overview of the photoelectron spectrum of nitrogen at hv=40 eV.
Figure 6.2 contains the valence shell photoelectron spectrum of CO. The molecular orbital configuration for carbon monoxide is valence isoelectronic with nitrogen, and hence has the same configuration, albeit without the gerade and ungerade symmetry labels. The adiabatic binding energy for each orbital is 14.013, 16.536, 19.674, 22.378, and 22.993 eV respectively. [44, 87, 88, 182, 188, 189] Our results were consistent with the spacing of these results, and our spectra were shifted to agree with the ground state ionization potentials. Figure 6.3 contains an enlargement of the CO$^+$($D^2\Pi$), and the CO$^+$($3^2\Sigma^+$) spectrum with the individual vibrations fitted.

Figure 6.2 Overview of the photoelectron spectrum of carbon monoxide at $h\nu=50$ eV.
Figure 6.3 The CO$^+$($D^2\Pi$) and ($3^{2}\Sigma^+$) spectrum with the individual vibrations fit.

As with the previous chapters, direct integration of the vibrational modes was not possible, so peaks were fitted with Gaussian functions in the commercially available software program Igor Pro™. [117] Gaussian curves were placed at the center of the each vibration, and the FWHM were held constant within each spectrum. The peaks were next fitted for intensity, and integrated for the area. The integrated areas of the peaks were used to calculate the vibrational branching ratios.

6.3.1.2 Vibrational Branching Ratio Curves

The vibrational branching ratios for $N_2^+$(X$^2\Sigma_g^+$) and (B$^2\Sigma_u^+$), and CO$^+$(X$^2\Sigma^+$) and (B$^2\Sigma^+$) are given in figure 6.4 below. Only the $v^+ = 1/v^+$ = 0 vibrational branching ratios are given even though all branching ratios have similar behavior. The two left frames
pertain to N$_2$ while the two on the right are for CO. The upper frames are for the (B$^2\Sigma^+$) electronic states, while the lower frames are for the (X$^2\Sigma^+$) states.

Figure 6.4 Comparison of the broad range behavior of vibrational branching ratio curves for N$_2$ and CO. First, both N$_2$ and CO show Franck-Condon breakdown over extended ranges that are normally assumed to be free of such behavior. This is the first time that photoelectron spectroscopy has revealed such behavior. Second, these valence isoelectronic systems show much different behavior in that the ground state of N$_2^+$ does not show a broad range excursion while the ground state of CO$^+$ does (bottom two frames). The situation is also reversed for the ionic excited states (top two frames).
The results presented in figure 6.4 have several important features. First, the broad range excursions of the diagonal top left and bottom right branching ratios. To put into context, the $3\sigma_g \rightarrow k\sigma_u$ shape resonance in the bottom left frame, $N_2^+ (\chi^2 \Sigma_g^+)$, is almost a δ-function on the energy scale of the frame. Second is that the valence isoelectronic states have profoundly different behavior, which can be seen by comparing the left frame to the equivalent right frame. Finally, compare the nitrogen ground and excited states. The broad nonresonant phenomenon is observed in the $N_2^+ (B^2 \Sigma_u^+)$ branching ratio, but nonexistent in the $N_2^+ (\chi^2 \Sigma_u^+)$ state.

![Diagram](image.png)

Figure 6.5 A typical branching ratio spectrum is shown for the $N_2^+ (A^2 \Pi_u^+)$ and $(C^2 \Sigma_u^+)$ states. Note that the high-energy region is relatively flat, in contrast to the data shown for the $N_2^+ (B^2 \Sigma_u^+)$ state shown in Fig. 6.4.
When we acquired these data, it was not clear why the ground state data were so different, and raises new questions. Is it that there are no Cooper minima, or that there are Cooper minima, but that there is no R-dependence? Similarly, the CO data are the “opposite” of the N$_2$ data, in that the excited data do not exhibit a broad range excursion, while the ground state data do. To help comprehend the nonresonant phenomena observed in the experimental vibrational branching, theoretical work was performed by our collaborators, and will be covered in the discussion section.

Branching ratio spectra were generated for the additional electronic states for nitrogen and carbon monoxide, but lack nonresonant phenomena. N$_2$ ($^2\Pi_u^{\pm}$) and (C$^2\Sigma_u^{-}$) display is an apparent shape resonance near threshold in figure 6.5, but there is no evidence of any broad-ranging non-Franck-Condon effect, such as was observed for the N$_2$ ($^2\Sigma_u^{\pm}$) state in figure 6.5.

6.3.2 Franck-Condon breakdowns in O$_2$ and NO

6.3.1.1 Photoelectron Spectra

Figure 6.6 contains the valence shell photoelectron spectrum of oxygen. The molecular orbital configuration for oxygen is $(2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^2$. The ionization potentials for the valence orbitals are 12.071, 16.101, 17.045, 18.171 and 20.296eV for the respective levels. [88, 189-192] Our results were consistent with the spacing of these results, and our spectra were shifted to agree with the ground state ionization potentials. Figure 6.7 contains an enlargement of O$_2$ ($^4\Pi_u$), ($^2\Pi_u$) and ($^4\Sigma_u^{-}$) spectrum with the individual vibrations fit.
Figure 6.6 Overview of the photoelectron spectrum of oxygen at $\hbar \nu = 30$ eV.

Figure 6.7 The $\text{O}_2^+$ ($a^4\Pi_u$, $A^2\Pi_u$, and $b^4\Sigma_g^-$) spectrum with the individual vibrations fit.

Figure 6.8 contains a spectrum for a selected region of nitric oxide. The entire valence region was not collected as part of my experiments. Figure 6.8 encompasses seven electronic levels comprised of 62 vibrations with the ionization potentials 15.667,
16.561, 16.863, 17.586, 17.811, 18.319, and 18.360 eV. The valence molecular orbital configuration for nitrogen is \((2\sigma)^2(2\sigma^*)^2(3\sigma)^2(2\pi)^4(2\pi^*)^1\). Our results were consistent with the spacing of these results, and our spectra were shifted to agree with the ground state ionization potentials. [193-195]

![NO photoelectron spectrum at hv=35eV](image)

Figure 6.8 A selection of the NO spectrum with the individual vibrations fit.

### 6.3.1.2 Vibrational Branching Ratio Curves

The vibrational branching ratios for \(O_2^+(X^2\Pi_g), (b^4\Sigma_g^-),\) and \((B^2\Sigma_g^-)\) are given in figure 6.9. Even though one branching ratio is given for each electronic state, all branching ratio are analogous in behavior. All three frames contain resonant behavior as
predicted by Braunstein. [61, 62] $O_2^+(X^2\Pi_g)$ presents with multiple resonances located
the excitation energies of 27 eV, and 42 eV.

Figure 6.9 A typical branching ratio spectrum is shown for the $N_2^+(A^2\Pi_u^+)$ and $(C^2\Sigma_u^+)$
states.

Cooper minima for in several electronic states of nitric oxide, but the excursions
in the vibrational branching ratios are at least an order of magnitude weaker than for the
$N_2$ and CO cases. There are many partial waves contributing, which could conceivably
attenuate the bond-length dependent effects that might be limited to a single $l$-wave, but the same might be said for CO.

Figure 6.10 The experimental and theoretical vibrational branching ratios for several electronic states of nitric oxide. Note that the scaling for the branching ratios is different for the experimental and theoretical branching ratios of each electronic state, and there is an offset of the baseline for the vertical axis.
6.4 Discussion

For most small molecular systems, the low-lying ion states are well described by a single configuration picture, where significant changes in configuration mixing as a function of geometry are not expected until considering higher lying electronic excited states. Such states are often formed as a mixture of simple inner valence hole states and one-particle two-hole states where the holes are formed in outer valence orbitals. To illuminate what is occurring, a detail analysis was performed on N₂ and CO theoretical measurements were performed as described in chapter 4 by Prof. Robert Lucchese.

![Figure 6.11 A comparison of the photoionization (blue square), fluorescence (red circle), [12, 78, 79] and Schwinger variational (green line) [12] N₂⁺(B²Σ_u⁺) vibrational branching ratios.](image)

Lucchese [196] proposed an alternative presentation of vibrational branching ratios, which could be directly related to the logarithmic derivatives of the cross section with respect to bond length. The result is a method to compare the breakdown of the
Franck-Condon approximation across systems with differing frequencies and bond shifts upon ionization. The broad range non-Franck-Condon nonresonant behavior could be analyzed within the Cohen-Fano structure. [197] Photoelectrons emitted from more than one atomic center can exhibit interference effects associated with Young's double slit experiment. [198] Evidence of interference phenomena may be seen from the total cross section, $\sigma$, defined as

$$\sigma = \sigma_0 [1 + (\sin kR)/kR],$$  \hspace{1cm} (6.1)

where $\sigma_0$ is the atomic photoionization cross-section (for a hydrogen-like atom of atomic number $Z^*$), $k$ is the electron wave vector and $R$ the internuclear distance. The recent work by Canton et al. [199] suggests that having non-identical centers, the interferences should differ from those coming from homonuclear molecules (just like having two different slits in the Young's experiment), but that coherent emission of the electron wave is still possible given a sufficiently delocalized ionized molecular orbital over the two nuclei.

For $N_2$ and CO ionization, the partial-wave cross sections were found to have an interference pattern similar to a Cohen-Fano interference, which can be related to molecular Cooper minima. By making a comparison between the Cohen-Fano interference phenomena and the molecular Cooper minima in the photoionization of diatomic molecules, these two descriptions are connected by the fact that the partial-wave matrix elements obtained from decomposition of the plane-wave matrix elements used in the Cohen-Fano analysis also have energies at which they change sign which is the characteristic of a Cooper minimum.
The result of the theoretical analysis gives some relatively straightforward guidance in the interpretation. One question that we wished to answer was why the CO\(^+\left(B^2\Sigma^+\right)\) vibrational branching ratio exhibits a pronounced deviation from Franck-Condon behavior while the N\(_2\)\(^+\left(B^2\Sigma_u^+\right)\) curve does not. The Schwinger variational calculations by Lucchese identify that the major contributor to the excursion observed for CO is a continuum partial wave with \(l=4\) and \(m=0\). However, for N\(_2\), an \(l=4\) partial wave is not possible owing to symmetry. The electron is ejected from the 3\(\sigma_g\) orbital, so dipole selection rules constrain the final orbital (even a continuum orbital) to have ungerade symmetry. Thus, an \(l=4\) partial wave cannot be a component of the final state wavefunction for N\(_2\), while it is allowed for CO, which lacks inversion symmetry.

However, it should be noted that the theoretical treatment finds that not all of the non-Franck-Condon effects, which emerge, are so easily explained, and in some cases, multiple partial waves are responsible. Thus, not all of the observed behavior can be broken down into qualitative explanations. With that said, the work reported here, including the result reported for NO and O\(_2\), represents a starting point, as these results are among the first experimental guideposts which can help guide future work in disentangling the relatively complex picture that currently exists.
Chapter Seven: Conclusions and Outlook

This work presented in this thesis has demonstrated that fundamental spectroscopic approximations are not always valid, and that photoionization provides a useful means of exploring the validity of the Franck-Condon approximation, specifically. By exploiting both experiment and theory techniques, insights can be revealed about molecular photoionization dynamics by focusing on the sensitivity of the ionization dynamics on changes in molecular geometry. By employing the strategy of using the high brightness of a third generation synchrotron, and high-resolution photoelectron spectroscopy, the study of vibrationally resolved spectra over a broad energy range, di-, tri-, and polyatomic species can be probed for resonant and nonresonant effects. A novel nonresonant mechanism for non-Franck-Condon behavior was discovered for ICN, a chemically-induced nonresonant coupling originating from geometry-dependent electronic structure changes in the initial state wavefunction. For N₂ and CO ionization, the partial-wave cross sections were found to have an interference pattern similar to a Cohen-Fano interference, which can be related to molecular Cooper minima by the fact that the partial-wave matrix elements obtained from decomposition of the plane-wave matrix elements used in the Cohen-Fano analysis also have energies at which they change sign which is the characteristic of a Cooper minimum. The result is fundamental experimental guideposts are established for the study of future systems. While unable to produce spectra of nucleobases with sufficient vibrational resolution to study photoionization dynamics, I have shown it is experimentally possible to produce partially vibrationally resolved spectra of large, asymmetric systems, forming the basis for a variety of future studies.
The results of these experiments can be extended into other systems. Large, asymmetric systems such as halogenated thiophenes, and pseudocyanide groups such as acrylonitrile would make excellent candidates. By improving the internal chamber design, and sample vaporization, improved vibrationally resolved spectra of nucleobases should become possible.
References


167. Urano, S., X. Yang, and P.R. LeBreton, *UV photoelectron and quantum mechanical characterization of DNA and RNA bases: Valence electronic


### Appendix: Tables of Nucleobase Vibrations from Fits

**Table A.1 Adenine at hv=21.2eV**

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Vita

David Adam Hardy was born 1983 in Akron, Ohio. He grew up in Norton, Ohio. He graduated from Norton High School, Norton, Ohio in 2001. He attended The University of Akron in Akron, Ohio, where he received a Bachelor of Science degree in chemistry. He is an Eagle Scout. His interests include antique razor restoration and racquetball. In December 2012, he will receive the degree of Doctor of Philosophy.