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Vibrational-Rotational-Electronic Correlations in Molecular Photoionization.

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VIBRATIONAL-ROTATIONAL-ELECTRONIC CORRELATIONS IN MOLECULAR PHOTOIONIZATION

A Dissertation

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

in

The Department of Physics and Astronomy

by

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DOCTORAL EXAMINATION AND DISSERTATION REPORT

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It is a profound and necessary truth that
the deep things in science are not found because they are useful:
they are found because it was possible to find them.

Robert Oppenheimer (1904 - 1967)
ACKNOWLEDGMENTS

There is a knack to training graduate students, in addition to it being a time consuming and an arduous task. All the same, it is an ability that seems to come easily to Professor Erwin Poliakoff. There is no doubt in my mind that I owe him a large debt of gratitude for the time (and money) he has invested in me, to help me realize my goals.

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ABSTRACT

Using the method of detecting dispersed fluorescence from electronically excited photoions, measurements of their vibrational and rotational distributions over a 200 eV photon energy range are presented. The vibrational distributions following 2σ_u^-1 photoionization of N_2 show a non-Franck-Condon behavior over a very broad energy range of nearly 100 eV. Comparison of these new results with detailed theoretical calculations of Wang & McKoy allow the interpretation of this Franck-Condon breakdown as arising from a dependence of Cooper minima on molecular bond length. The results highlight the molecular character of photoionization dynamics, even deep in the ionization continuum. For a detailed investigation of the R-dependence of the Cooper minima, rotational state resolved measurements into alternative vibrational channels are determined over the same photo-excitation energy range as was carried out for the vibrationally resolved measurements. By simultaneously determining the vibrational and rotational energy deposition into the photoion, we investigate vibrational-rotational-electronic (V-R-E) coupling over a broad range of electron energy. These N_2 results help better characterize the underlying dynamics of photoionization and the role of molecular Cooper minima. Vibrational distribution measurements are presented for the iso-electronic species CO over a similar energy range. The effectiveness of dispersed fluorescence measurements as a survey tool for picking out near-edge structure is demonstrated in the results of K-shell photoionization measurements of N_2.
CHAPTER 1

INTRODUCTION

From the time of the prize-winning study of the photoelectric effect, the response of matter to electromagnetic fields has been used to study and understand the properties and structure of materials. Electromagnetic forces and quantum-mechanical effects govern the motion of electrons and nuclei, and are responsible for the cohesion of atoms and molecules and their mutual interplay and reactions. The interaction of electromagnetic fields with these particles is thus fundamental to understanding and interpreting the properties of matter. Stated otherwise, in the context of this dissertation, the study of interaction of light with atoms and molecules is an essential source of information on their structure and dynamics.

1.1 Molecular Photoionization

Among the processes that can follow absorption of a photon by molecules, ionization is the simplest, where in the fragments consist of the ejected photoelectron and the remaining photoion. Consider, for example, the ionization of a generic molecule “M” following interaction with a beam of monochromatic light (with sufficient energy to ionize the molecule):

\[ M + h\nu_{\text{exc}} \rightarrow (M)^* \rightarrow (M^+)^* + e^- . \]  

(1-1)
In this half-collision view of the ionization process [1], the decay products of the collision complex (M)* contain information pertaining to the complex formed following the absorption of a photon. Consequently, studying the fragments provides a window to understanding the evolution of the molecule plus photon system. Conservation laws imply that the energy, angular momentum and parity of the fragments is complementary, and that the fragments’ abundances are equal [2]. Hence, measurements on either of the fragments – the photoion or the photoelectron – can yield information on the dynamics of photoionization. Photoelectron spectroscopy (PES) involves measuring the energy, angular distribution, and spin of these photoelectrons as a method of extracting information on the molecular orbital from where it was ejected. Measurements on the photoions sidesteps resolution limitations of conventional PES techniques, and is the method used for the high resolution studies described in this dissertation. We take advantage of the fact that after ejection of an electron, the residual ion created is in an excited ionic state that does not undergo fast decay processes, such as dissociation or internal conversion and thus fluoresces:

\[(M^+)^* \rightarrow (M^+) + h\nu_{\text{fluorescence}} \cdot (1-2)\]

Fluorescence from these excited photoions, i.e. (M^+)*, contains information about the vibrational and rotational energy that was deposited by the departing electron on the residual photoion. A particularly advantageous aspect of fluorescence detection technique is that modern tunable light sources, namely, synchrotron radiation, can be exploited as an excitation source without sacrificing the level of resolution required of comprehensive studies of ionization dynamics [3]. The results of such a use of the
synchrotron radiation source at the Center for Advanced Microstructures and Devices (CAMD), where high resolution measurements were made over a broad spectral range, are presented here.

1.2 Motivation & Overview

In the overall scheme of studying scattering dynamics, photoionization has a special place primarily because of its relative simplicity. The initial photoabsorption creates, almost instantaneously, an interaction complex that then decays into its fragments as represented in Eq. (1-1). In the perturbation theory limit, the entrance channel is unaffected by the complexities of collision physics [1]. All the action is in the exit channels where the fragmentation takes place. In molecules this raises two important aspects of ionization dynamics. One component to the photoionization process involves the initial ejection of an electron from a molecular orbital. The step that follows the removal of the electron involves the second aspect, viz., its interaction with the anisotropic fields of the ion while escaping from the field of the molecule. So the electron carries with it the features of the molecular orbital that it was ejected from, and the dynamics of the rescattering process that it underwent following interaction with the molecule’s fields. These issues address the motivation for such photoionization studies, which is to probe not only aspects of the initial state of the molecule’s electronic structure but also the ‘final state’ aspects – the dynamics of the ejection of the outgoing photoelectron.

This study can be broadly divided into two parts, reflecting the hierarchy of complication and detail. At the coarse level of detail are the vibrationally resolved spectra that are crucial for information about the structure and bonding of the ions in that state [2]. In such interpretations of vibrational spectra from photoionization or photodetachment data, it is usually assumed that the vibrational intensities are
governed by the Franck-Condon approximation. It is based on the idea that electronic transitions occur very quickly, during which time the nuclei do not have sufficient time to move [4], implying that electronic and vibrational motion are not correlated [5]. Hence, in ejecting an electron by photoabsorption, the ratio of cross sections for ionization to alternative vibrational levels is predicted to be constant with photon energy. But the results reported here will show that it is not so in all cases; we see a coupling between electronic and vibrational motion which in one case, is global in extent. The first such observation of broad-range Franck-Condon break-down, these vibrational-electronic correlations extend over an excitation energy range of hundreds of electron-volts. This is surprising because it is generally expected that molecular character in photoionization dynamics is lost at high photoelectron energies and can be regarded as being atomic-like. Recognizing and quantifying the extent of such molecular effects can serve at least to refine and test many aspects of our present day understanding of molecular photoionization.

The mentioned results of the study at the coarse level of detail motivated the second part of this dissertation, where it was necessary that we dig deeper and into the finer level of detail, and study the distribution of rotational state populations following photoionization. The rotational structure of different vibrational levels were then compared so as to investigate the underlying dynamics of the coupling observed in the vibrationally-resolved measurements. With the help of detailed theoretical calculations to interpret the experimental measurements, the vibrational-rotational-electronic (V-R-E) correlations observed were found to be a result of bond-length dependent Cooper minima that exist deep in the ionization continuum. All of this highlights the vividly molecular nature of photoionization dynamics, even
for scattering energies well in excess of those deemed relevant (i.e., energies on the order of 4 eV).

Chapter 2 accounts the basics and background that address the current expectations of the ionization processes. The discussion is confined to ionization phenomenon that are relevant to the samples considered in this study. The chapter ends with an outline of the theoretical basis of the calculations of K. Wang and V. McKoy. The results of their calculations are later used to interpret the results obtained from my measurements.

Chapter 3 details the experimental method; the tools employed, data acquisition methods, procedures for data analysis and data reduction. The account simultaneously presents the advantages and limitations of the methods employed with their relation to the results obtained in this dissertation.

The results are presented in Chapter 4 and include vibrationally and rotationally resolved data for 2σ_u^-1 photoionization of N_2. These results are compared with the calculations of Wang and McKoy for the purposes of interpreting and understanding the central aspects of the photon-molecule interactions. Vibrationally resolved measurements of 4σ^-1 photoionization of CO are presented, to serve as a contrast to the behavior of its isoelectronic partner N_2. Results of extending this technique of detecting dispersed fluorescence to probe K-shell ionization of N_2 are discussed in the last section of the results chapter. The study focuses on characterizing channel coupling effects in the core-electron ionization dynamics that are magnified by the presence of a shape resonance [8]. The motivation is that quantifying core-hole/valence-hole channel coupling effects can extend the advantages of fluorescence spectroscopy to K-edge studies of molecular structure [9, 10].
Chapter 5 attempts to summarize these new results and the implications of the observed vibrational-rotational-electronic coupling. The section closes with a brief suggestion for possible future work.
CHAPTER 2

BACKGROUND

The quantum theory of molecules as worked out by Max Born and Robert Oppenheimer turned out to be an enduring contribution [11]. It involves an important approximation that has allowed molecular spectroscopists to interpret their spectra, and its significance is obvious from the number of times this approximation is invoked. The Born-Oppenheimer approximation, after neglecting the spin-orbit coupling, leads to the separation of electronic and nuclear motion, thereby allowing one to solve relatively easily the Schrodinger equation, and hence explain, in principle, all of chemistry and spectroscopy [12]. Within this framework of the Born-Oppenheimer approximation, we will now attempt to characterize some qualitative aspects to the parametric interdependencies between nuclear motion (molecular vibrations and rotations) and electronic motion.

2.1 The Franck-Condon Approximation

Let us consider right away the ejection of an electron from a molecule and examine the classical expectations of the process before tackling its quantum mechanical aspects. Considering that the electron mass is much smaller than that of nuclei, one would expect no substantial kinematic effect of the electron “kicking off” from the nucleus. For example, conservation of linear momentum suggests that the change in nuclear kinetic energy is of the order of a few thousandths of an eV when
the electron is ejected with an energy of 100 eV from a nitrogen molecule. The primary implication is that the interaction of the outgoing electron with the residual photoion is negligibly small. Keeping with this classical picture, as had been postulated originally by Franck [4], the target molecule is assumed to be frozen at the equilibrium position. Immediately following the electron ejection, the unchanged positions of the nuclei are no longer the equilibrium positions in this new ionic state. Thus, the nuclei will now vibrate about the new ionic equilibrium positions. Knowing the vibrational modes that are thus excited is tantamount to understanding the nature of the ionic state produced following the ejection of an electron. The change produced in the molecule following the removal of an electron also reflects the bonding character of the electron removed [2]. So, the simplifying assumption that the “kick-off” energy of the electron does not determine the amplitude and frequency of vibrations of the final ionic state has a direct consequence to interpreting ionization data.

The quantum description of photoionization, as will be seen, provides the same prediction as given by the qualitative argument above [5,11]. Let us consider first the expression for the electric dipole transition matrix element for a transition from some initial level \(| i \rangle\) to an electronic continuum state \(| \varepsilon \rangle\):

$$D (i \rightarrow \varepsilon) = \langle \varepsilon | d | i \rangle. \quad (2-1)$$

Following the Born-Oppenheimer approximation, and neglecting the rotational motion of the molecule, the total eigenfunctions can be represented as a product of the vibrational wavefunction, \(\chi(R)\), and an electronic wavefunction, \(\phi(r, \theta, \varphi, R)\), where ‘R’ represents the internuclear separation and ‘r’, ‘\theta’ and ‘\varphi’, represent the electron positions in spherical coordinates. Thus, we have
Furthermore, the dipole operator can be resolved into its electronic and nuclear parts, and thereby, \( \mathbf{d} = \mathbf{d}_{\text{nuc}} + \mathbf{d}_{\text{el}} \). The transition matrix element can now be written as

\[
D (i \to e) = \langle \phi_e \chi_e | \mathbf{d} | \phi_i \chi_i \rangle. \tag{2-2}
\]

The first term goes to zero because electronic eigenfunctions belonging to different electronic states are orthogonal to one another. In the second term, one can integrate over the electron coordinates to reduce the expression to

\[
D (i \to e) = \langle \phi_e \chi_e | \mathbf{d}_{\text{nuc}} | \phi_i \chi_i \rangle + \langle \phi_e \chi_e | \mathbf{d}_{\text{el}} | \phi_i \chi_i \rangle. \tag{2-3}
\]

The first term goes to zero because electronic eigenfunctions belonging to different electronic states are orthogonal to one another. In the second term, one can integrate over the electron coordinates to reduce the expression to

\[
D (i \to e) = \langle \phi_e \chi_e | \mathbf{d}_{\text{nuc}} | \phi_i \chi_i \rangle + \langle \phi_e \chi_e | \mathbf{d}_{\text{el}} | \phi_i \chi_i \rangle = \langle \chi_e | [\mathbf{D}_{\text{el}} (R)] \chi_i \rangle. \tag{2-4}
\]

It is at this point that we make the Franck-Condon approximation, namely, that the electronic transition probability, \( \mathbf{D}_{\text{el}} (R) \), is a *slowly varying* function of the internuclear separation \( R \). As a result we may now replace the exact electronic transition probability with an average value determined for some equilibrium internuclear separation \( R_e \). We then have

\[
D (i \to e) = \langle \chi_e | [\mathbf{D}_{\text{el}} (R_e)] \chi_i \rangle. \tag{2-5}
\]

The transition probability and hence the intensity is proportional to the square of the above expression, i.e.
If we now consider the ratio of the transition probabilities or, as in this case, ionization cross sections, to alternative vibrational levels of the same final electronic state, we get

\[ \frac{\sigma (v_i \rightarrow v_{e_1})}{\sigma (v_i \rightarrow v_{e_2})} = \frac{|\langle \chi_i | \chi_{e_1} \rangle|^2}{|\langle \chi_i | \chi_{e_2} \rangle|^2} = \frac{q_{i \rightarrow e_1}}{q_{i \rightarrow e_2}}. \]  

(2-7)

where \( (q_{i \rightarrow e}) \) is the square of the overlap of the vibrational wavefunctions, and is also referred to as the Franck-Condon factor. This overlap integral, therefore, determines the intensity distribution in the emission or absorption band of an electronic transition and so lends itself to being a vibrational selection rule of sorts [2]. As argued in the classical description, the relative rates of photoionization from one initial bound state to alternative vibrational levels of a final electronic state is independent of the incident photon energy.

The important procedure of interpreting intensities of vibrationally-resolved partial cross sections, as in extracting accurate ionic potential surfaces [13], thus rests on having a clear understanding of the vibrational aspects of photoionization. It is therefore important to characterize the conditions for the validity of the Franck-Condon approximation, particularly since it is normally invoked for such purposes as those just mentioned. One method for characterization would be to measure the intensity distribution of the vibrational structure in an electronic transition as a function of the excitation photon energy. Any variation in the vibrational branching
ratios would then indicate an exception to the approximation and we shall now address their implications.

2.2 Franck-Condon breakdown

Observations of non-Franck-Condon (non-FC) effects in the vibrational branching ratios stem from the invalidity of replacing the exact electronic transition probability with an average value. In other words, Franck-Condon breakdown results from a strong \( R \) dependence of \( D_{\text{el}}(R) \). From the expression for the electronic transition probability,

\[
D_{\text{el}}(R) = \langle \phi_e | d_{\text{el}} | \phi_i \rangle ,
\]

we can see that its \( R \) dependence is derived from that of the initial and final state electronic wavefunctions \( \phi_i \) and \( \phi_e \). Categorizing them as initial and final state effects, a strong \( R \) dependence of \( \phi_i \) or \( \phi_e \) (or both) can result in non-FC effects in photoionization. It has so conspired that the non-Franck-Condon effects studied so far have been due to ‘final state’ effects [7, 13]. Electronic autoionization and shape resonances have been shown to result in Franck-Condon breakdown [7, 14], and both are ‘final state’ effects that follow from resonant excitation. On the other hand, predictions of non-FC behavior due to initial state effects have been made [15], as in the special case of photoionization of hydrides in Rydberg target states [16]. The experimental results reported in this dissertation deal primarily with the non-FC behavior that arises from the presence of Cooper minima, and so lend themselves to being described as an ‘initial state’ effect. The influence of Cooper minima on molecular vibrations over a wide spectral range has never been studied before [15] and is the centerpiece of the current study. To place this work in context,
measurements of shape-resonance-induced effects are presented along with Cooper-minima-induced non-FC effects. The salient features of Cooper minima and shape resonances in photoionization dynamics are briefly reviewed in the following two sub-sections.

2.2.1 Cooper minima

Early photoionization experiments on alkalis reported minima in the cross-sections measured as a function of photon energy [17]. The explanation given by Bates [18] and Seaton [19] was that there was a great deal of cancellation in the outer shell alkali-metal dipole transition matrix elements that resulted in some matrix elements going to zero, thus causing a minimum in the cross-sections. To illustrate the argument, consider again the expression for the dipole transition moment given by Eq.(2-8). After separating the electronic wavefunctions into its radial and angular parts, integration over the angular coordinates (in the central-field approximation) yields the selection rules for the change in orbital angular momentum quantum number and orbital magnetic quantum number for the electronic transition. The transition moment now reduces to evaluating the radial dipole matrix element,

$$R_{\ell+1} = \int_0^\infty u_{n\ell}(r) r u_{n+1\ell \pm 1}(r) \, dr,$$ (2-9)

where \((u_{n\ell} / r)\) and \((u_{n+1\ell \pm 1} / r)\) are the radial parts of the initial and final state electronic wave functions. The dynamic variations in the cross-sections are determined by the nature of \(u(r)\), and can cause their \(r\)-weighted overlaps to change sign as a function of energy and go through a zero.

It was later shown by Cooper that the accidental cancellation described above was a general occurrence, by predicting and categorizing such minima in the
photoionization cross-sections of rare gases and metals [20, 21]. Such a change in
the sign of the dipole matrix element as a function of photon energy is now referred
to as a Cooper minimum. Consider now the contrasting examples of photoionization
of Ne and Ar used in the original discussion [20]. The radial wavefunction for the
outer atomic shells, Ne(2p) and Ar(3p), are shown in Fig. 2.1 along with their
continuum $d$-wave radial wavefunction for zero kinetic energy.

![Wavefunctions](image)

Figure 2.1: Outer subshell radial wavefunctions and $d$-waves at zero kinetic energy
for Ne and Ar, from reference [20].

It can be seen that the $d$-wave matrix element ($R_{l+1} = 2$), is positive for Ne but
negative for Ar. The wavefunctions for argon have opposite signs in the overlap
region, which is why the dipole integral is negative at $\varepsilon = 0$. The effect of increasing
the continuum energy $\varepsilon$, is that the nodes of the $d$-wave get drawn in towards the
origin, and the effects of the contribution from the negative lobe of the continuum
wavefunction starts to show. Plotted in Fig. 2.2 is the value of the integral $R_{l+1} = 2$
as a function of \( \varepsilon \), showing the overlap interval for \( \varepsilon = 0 \) and its change with increasing electron energy.

The behavior in Ar is determined by the effect of decreasing the wavelength of the continuum \( d \)-wave. At some point the contribution to the dipole integral from the negative lobe of the \( d \)-wave cancels out that of the positive lobe, resulting in a zero. In the case of both neon and argon, the continuum wavefunctions (\( d \)-wave) are similar oscillatory functions, but the initial states are quite different. It is illustrative of the conditions for the occurrence of Cooper minima; they are a quirk of the initial state wavefunction and its form in the region near the edge of the atom [22].

Cooper minima not only modulate oscillator strengths but also profoundly affect photoelectron angular distributions and have been studied extensively [6, 23]. They have also been found in a host of molecular systems, where their effects on photoelectron angular distributions have been well documented [24, 25]. The key difference in molecular systems from atoms is that the familiar selection rule \( \Delta \ell = \pm 1 \) (for single-atom optical transitions) does not apply for molecules[1]. This is because angular momentum can be exchanged between the outgoing photoelectron and the molecule’s rotational motion, so that the photoelectron is no longer restricted to \( \Delta \ell = \pm 1 \). The presence of a “non-zero internuclear distance” thus has a crucial role to

![Graph showing the overlap interval for different electron energies.](image)

**Fig. 2.2** Matrix elements for \( p \rightarrow d \) transition in Ne and Ar, from reference [20].

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play in ionization dynamics [26], and is part of the motivation for studying the influence of molecular vibrations (otherwise, changing internuclear distance \( R' \)) on Cooper minima. This study covers a wide spectral range that has never been investigated before, and reflects the effectiveness of the experimental method employed. For a complete understanding and interpretation of such broad-range studies, an effective theoretical machinery is indispensable. The theory used to explain the experimental results is discussed in a later section.

2.2.2 Shape resonance

The existence of quasi-bound states in the ionization continuum has played a prominent role in molecular photoionization [7]. These quasi-bound states temporarily trap the photoelectrons in a potential barrier, and lead to resonance features in photoionization processes. In molecular systems, centrifugal barriers were found to play the role of trapping otherwise free electrons, leading to what are now known as shape resonances.

The basic properties of a shape resonance can be illustrated using a model potential shown in Fig. 2.3. The horizontal axis represents the distance of the photoelectron from the center of the molecule. The model potential incorporates the basic ingredients for the existence of quasibound states. There is an attractive inner potential well at small distances, which is separated from the outer region by a potential barrier. The wavefunctions, plotted for three different continuum energies, demonstrate the effect of the barrier on the photoelectron continuum wavefunction. For non-resonant energies (i.e. \( E > E_r \) or \( E < E_r \)), the inner well does not support a quasibound state and the wavefunction has a relatively small amplitude in the inner well. At \( E = E_r \) the well now supports a quasibound state and the wavefunction amplitude is now greatly enhanced in the well region. In this resonant condition, the
wave function decays exponentially in the barrier region, so that if the barrier were extended to $r \to \infty$, a true bound state would lie near this energy. As in any resonance phenomenon, there is a phase change of $\pi$ in the continuum wavefunctions when the energy is tuned through the resonant energy. One can now deduce the physical effects of the resonance properties just discussed.

![Figure 2.3: Model potential describing the effect of a barrier on the continuum electron wavefunction.](image)

The enhancement of the wavefunction in the inner well region for the resonance condition translates to a good overlap with initial bound states. The result is a strong modulation of the oscillator strengths when tuned through the resonance energy. The rapid change in the eigenphase in turn affects the photoelectron angular distribution. The barrier that temporarily traps the photoelectron is a centrifugal barrier, and so it supports a quasibound state only for specific $\ell$ components and, in
molecular fields particularly, the electron motion is restricted only in certain
directions of certain ionization channels. Specific examples of K-shell and 3σ_g
photoionization of N_2 that will be discussed again later have demonstrated excellent
qualitative agreement between theoretical calculations and experimental spectra.

The breakdown of the FC principle arises from the sensitive dependence of
the resonance and its properties on the molecular geometry. In the case of diatomics,
the resonance energies and lifetimes are sensitive functions of the internuclear
separation R. This is illustrated in Fig. 2.4 using the very same model potential,
where the width of the well serves to represent the internuclear distance.

![Figure 2.4: Effect of changing internuclear separation (represented by the well
width) on the energy position of the resonance.](image)

Such a dramatic dependence of the continuum final state wavefunction on the
internuclear separation is a recipe for non-FC effects. Notice that for a larger
internuclear separation (well width = 3.1), the resonance shifts to lower energies as
the inner well is now more attractive. For smaller internuclear separation (well width
= 2.9), the resonance energy is shifted up because of a more repulsive inner well.
Different vibrational states sample different ranges of internuclear separation, and
hence, ionization to alternative vibrational levels in the vicinity of a shape resonance
will produce non-FC vibrational distributions. A particularly illustrative example of
Franck-Condon breakdown are the vibrational branching ratios obtained for $N_2$ photoionization via photoelectron spectroscopy [27]. Plotted in Fig. 2.5 is the energy dependence of the vibrational branching ratios covering the $3\sigma_g \rightarrow k\sigma_u$ shape resonance region in $N_2$.

![Franck-Condon prediction](image)

Figure 2.5: Franck-Condon breakdown in the $3\sigma_g^{-1}$ photoionization of $N_2$. Experimental (error bars) and theoretical (broken curve) are from references [27] and [28], respectively.

It is useful to note the spectral extent of the resonance, viz. on the order of 10 eV, as our results will be compared to it later. This non-FC behavior, comes about because of the sensitivity of the continuum resonance to changing internuclear separation, as demonstrated in Fig. 2.4, and hence shape resonance-induced non-FC effects can be classified as being a 'final state' effect.

To be able to interpret any experimental measurements of FC-breakdown, one has to examine the underlying dynamics of photoionization. Characterizing and identifying phenomena in the ionization continuum requires a careful look at the angular momentum partitioning between the photoelectron and the photoion. The rotational effects involved in photoionization carry the details of the partial wave composition of the photoelectron continuum. This is what motivated the subsequent
rotationally-resolved measurements made over the range of the observed non-FC effects. The theoretical machinery that examines in detail the division of angular momentum between photoionization fragments is discussed now in the next section.

2.3 Details of the theory

To gain physical insight into the processes occurring during photoabsorption and the eventual escape of the photoelectron, let us begin with a schematic for the general photoemission process in diatomics [29], where nuclear spin has been neglected:

\[
\text{AB}(J_0, \pi_0) + h\nu (J_p=1, \pi_p=-1) \rightarrow \text{AB}^+(J^+, \pi^+) + e^- (J_e=\ell +1/2, \pi_e=(-1)^\ell) . \quad (2-10)
\]

As mentioned earlier, the outgoing electron can transfer angular momentum to the rotational motion of the ion core. It can be viewed as a torque being exerted on the escaping photoelectron and consequently transitions to continuum states of successive \(\ell\) are possible. The allowed \(\ell\) values can be determined from conservation of total angular momentum (excluding nuclear spin) which requires that

\[
J_0 + J_p = J^+ + J_e , \quad (2-11)
\]

and from parity conservation (i.e. the electric dipole operator only connects states of opposite parity) [30]:

\[
(-1)^{J_0+1} = \pm (-1)^{\ell + J^+} . \quad (2-12)
\]
It is now convenient to assume that the wavefunctions of AB and AB\(^+\) follow one of three well known angular momentum coupling schemes. For a \(\Sigma \rightarrow \Sigma\) transition of interest here, both initial and ionic states can be best described by the Hund's case (b) coupling scheme [12]. It allows us to neglect electron spin and define angular momentum selection rules for the allowed dipole transitions [30] as

\[
\Delta N = 0, \pm 1, \pm 2, ..., \pm (\ell+1), \quad (2-13)
\]

where \(N\) is the total angular momentum excluding electronic spin (i.e. \(N = J - S\)). In addition, homonuclear diatomics have a center of symmetry. As a result, the electronic wavefunctions can be divided between those that remain unchanged, or only change sign when reflected through the center. Consequently, for a \(\Sigma_{g}^{+} \rightarrow \Sigma_{u}^{+}\) transition in \(N_{2} \rightarrow N_{2}^{+}\), the allowed values will now be given by Eq. (2-14) for only even angular momentum \(\ell\) [30]:

\[
\Delta N = \pm 1, \pm 3, ..., \pm (\ell+1). \quad (2-14)
\]

In the details of the calculations of ionization cross sections, a key quantity is the photoelectron matrix element and particularly its dependence on internuclear distance. Indeed, to account for non-FC effects, the R-dependence in the bound-free transition moment should be included in the calculations. Only the essential features of such a calculation will now be discussed.

The cross section for ionization of a level \(J_0\) of the initial state to a \(J^{+}\) of the ion, \(\sigma (J_0 \rightarrow J^{+})\), can be written as [31]
\[
\sigma(J_0 \rightarrow J^+) \propto \sum_{\ell_m} \rho_{M_{J_0} M_{J_0}} \left| C_{\ell m} \left( M_{J_0} , M_{J^+} \right) \right|^2 ,
\]  

(2-15)

where \( \rho_{M_{J_0} M_{J_0}} \) is the population of the \( M_{J_0} \) sublevel of the initial state. For a \( \Sigma \rightarrow \Sigma \) transition of interest here, the coefficients \( C_{\ell m} \left( M_{J_0} , M_{J^+} \right) \) take the form [32],

\[
C_{\ell m} \left( M_{J_0} , M_{J^+} \right) = C_{\ell m} \left[ \sum I_{\ell \lambda \mu} \left( \begin{array}{ccc} N^+ & N_0 & N_t \\ -\Lambda_+ & \Lambda_0 & \lambda_t \end{array} \right) \times \left( \begin{array}{c} N_t \\ 1 \\ \ell \end{array} \right) \right] ,
\]  

(2-16)

where \( I_{\ell \lambda \mu} \) is the vibrationally-averaged photoelectron matrix element between the initial state and the photoelectron continuum wavefunction. It contains a key quantity, the photoelectron matrix element, and is given by,

\[
I_{\ell \lambda \mu} = (-i)^\ell e^{i \eta t} \int dR \chi_{\lambda_+}^* (R) \ r_{fi}^{\ell \lambda \mu} \chi_{\lambda_0} (R) ,
\]  

(2-17)

where

\[
r_{fi}^{\ell \lambda \mu} = \left\langle \psi_{\ell \lambda} (r) \right| \mu \cdot \varepsilon \left| \psi_i (r, R) \right\rangle .
\]  

(2-18)

The partial wave components are obtained for the initial and final state wavefunctions by single-center expansions in spherical harmonics about \( k \) (the momentum of the outgoing wave in the laboratory frame). A rotation by the three Euler angles will then bring the laboratory-fixed frame in coincidence with the molecule-fixed frame [29]. The expression for the photoelectron matrix elements now reduces to
The point to note here is that $\ell \neq \ell'$ terms are brought about by the non-spherical molecular ion potential. This is not so in the central fields of atomic systems where conservation of the electron angular momentum allows only the $\ell = \ell'$ terms. For rotationally resolved studies, the crux of the scattering process is here in the description of the angular momentum coupling between the photoelectron and ionic core. In addition, a strong $R$ dependence of the photoelectron matrix element would invalidate a Franck-Condon factorization of an average value for the photoelectron matrix element. Consequently, the vibrationally averaged photoelectron matrix element $I_{\ell \lambda \mu}$ now allows us to see the underlying dynamics of the photoionization process, its dependence on the vibrational state involved, and how it evolves with energy. Since the experimental technique used here is only able to determine the final state rotational populations, the calculations need to consider all transitions terminating in a specific ion level $J^+$, which is achieved by integrating over all initial rotational levels $J_0$, i.e.

$$n_{J^+} = \sum_{J_0} \sigma \left( J_0 \rightarrow J^+ \right).$$

(2-20)

The results of these calculations carried out and provided by Wang and McKoy will be presented side-by-side with the experimental results, for the purposes of interpreting the results.

The calculations discussed are at the independent particle level, and so do not address multichannel effects [33]. Both Cooper minima and shape resonances,
are single channel phenomena and are adequately described by these calculations. The calculations assume the validity of the Born-Oppenheimer approximation [33], implying that the electronic-nuclear coupling discussed is a parametric coupling that reflects the parametric dependence of the electronic wavefunction on the internuclear distance.
CHAPTER 3

PRINCIPLES AND TECHNIQUES OF THE EXPERIMENTAL METHOD

When constrained by a lay person to summarize my experimental work in a sentence, I have found it telling to describe my work as watching a 'table-top' Aurora. Romanticizing is not all that is intended in such a description; watching the northern lights does amount to detecting fluorescence from molecules and atoms that were excited by primary and secondary cosmic ray particles. Monitoring the fluorescence from $\text{N}_2$ and CO molecules, following excitation under controlled conditions, is the technique used here to understand certain aspects of scattering dynamics. Going beyond the analogy, fluorescence spectroscopy has served as an effective high-resolution probe of photoionization [31]. Its distinction is that it can access high-resolution data over a wide range of ionization continua, made possible by synchrotron radiation sources [34].

3.1 Dispersed Fluorescence Method

Following photoionization, molecular ions can be formed in various different states. If any of these ionic states fluoresce, its spectrum is then a source of details of those states produced following the absorption of a photon. By monitoring the intensity of fluorescence from a particular quantum level of the photoion, we infer the rate of ionization to that particular quantum level [35]. Branching ratios are thus
Figure 3.1: Experimental method of detecting fluorescence compared to photoelectron spectroscopy. The simulated spectrum shows how the electron detection bandwidth is tied to the excitation bandwidth, while for fluorescence detection, \((h\nu_f)\), the band width is not coupled to \(\Delta E_{\text{exc}}\).
proportional to the ratios of fluorescence intensities between alternative quantum levels. We will use the process illustrated in Fig 3.1, namely, $2\sigma_u^{-1}$ photoionization of $\text{N}_2$, as an example to discuss the various aspects of the motivation for the experimental method used in this dissertation.

3.1.1 Fluorescence spectroscopy vs. Photoelectron spectroscopy

The ionization process in Fig. 3.1 involves the ejection of the $2\sigma_u$ electron, whereby the resulting ion $\text{N}_2^+(B^2\Sigma_u^+)$ decays to the ionic ground state by emitting a fluorescence photon. From the excitation-fluorescence sequence,

$$\text{N}_2(X^1\Sigma_g^+, v_0 = 0) + h\nu_{\text{exc}} \rightarrow \text{N}_2^+(B^2\Sigma_u^+, v^+) + e^-$$

$$\downarrow$$

$$\text{N}_2^+(X^2\Sigma_g^+, v'') + h\nu + v'', \quad (3-1)$$

it can be seen that the ionization process can be probed by energy analysis of the photoelectron (PES) or by energy-analyzed ionic fluorescence (dispersed fluorescence). The lower limit to the photoelectron energy resolution, as depicted in Fig. 3.1, is determined by the energy bandwidth of the photon source. The bandwidth requirements show that for vibrationally-resolved electron spectroscopy, the resolving power requirements are already almost $10^3$ for measurements at $h\nu_{\text{exc}} \approx 50\text{eV}$. On the other hand, the fluorescence bandwidth is determined solely by the lifetime characteristics of the fluorescing state. Thus the resolving power of the optical detection system is the limiting factor in dispersed fluorescence studies [3], where rotational spacing on the order of $4 \text{ cm}^{-1}$ can be routinely resolved [31]. For such rotational distribution measurements at $h\nu_{\text{exc}} \approx 200\text{eV}$, the ante is upped on PES, and the required resolving power of nearly $10^6$ is beyond the limits of current electron spectroscopy measurements at comparable excitation energies [36, 37].
resolving power requirements of the fluorescence measurements are not a function of the excitation bandwidth. Consequently, fluorescence measurements have a key advantage over traditional PES techniques when the excitation source has limited resolving power and tunability is critical.

An important obstacle to fluorescence measurements over a wide excitation energy range can be the creation of the fluorescing state through the decay of another excited ionic state [3]. This, in principle, can be the most daunting problem with fluorescence spectroscopy, but is not an issue in the molecular systems studied here.

3.1.2 Branching ratios from fluorescence intensities

As indicated earlier, the fluorescence intensity originating from a level is a measure of the rate of ionization to that level. Stated in terms of the number of fluorescence photons emitted per second, $I_{\text{exc-}\rightarrow\text{gr}}$, following an electronic transition from an excited ionic state to its ground state,

$$I_{\text{exc-}\rightarrow\text{gr}} = n_{\text{exc}} \cdot A_{\text{exc-}\rightarrow\text{gr}} ,$$

(3-2)

where $n_{\text{exc}}$ is the number of excited ions created following photoionization to that particular quantum state. The Einstein A coefficient for spontaneous emission, in the absence of degeneracy, can be shown [37] to be given by,

$$A_{\text{exc-}\rightarrow\text{gr}} = \frac{64 \pi v^3}{3hc^3} |D_{\text{exc-}\rightarrow\text{gr}}|^2 .$$

(3-3)
The central issue now, in using ratios of transition rates to determine \( n_{\text{exc}} \), is the calculation of the dipole transition matrix element, \( D_{\text{exc} \rightarrow \text{gr}} \). For vibrationally resolved measurements, we can use Eq. (2-7) to get vibrational branching ratios,

\[
\frac{\sigma_{v_1^+}}{\sigma_{v_2^+}} = \frac{n_{v_1^+}}{n_{v_2^+}} = \frac{I_{v_1^+ \rightarrow v_1'^+}}{I_{v_2^+ \rightarrow v_2'^+}} \cdot \frac{q_{v_2^+ \rightarrow v_2'^+}}{q_{v_1^+ \rightarrow v_1'^+}} \cdot \left( \frac{v_{v_2^+ \rightarrow v_2'}}{v_{v_1^+ \rightarrow v_1'}} \right)^3 .
\]  (3-4)

So, the fluorescence intensity ratios, scaled by a constant factor, provide the vibrational branching ratios. There is however an important caveat that needs to be added to the above analysis for vibrational branching ratios. Excited vibrational levels can decay via fragmentation or non-radiative internal conversions, and these rates could be different for different vibrational levels [38]. In such a case, Eq. (3-4) has to be modified by multiplying with the corresponding alternative depopulating rate [39]. For the present study, especially for \( \text{N}_2^+ (B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+) \) fluorescence, the quantum yields have been found to be unity [2, 40], and so are unaffected by such effects.

To calculate rotational branching ratios, the dipole transition matrix element has to be evaluated, this time taking into account the initial and final rotational states. Once again we begin by invoking the Born-Oppenheimer approximation and write the initial and final state wavefunctions as a product of an electronic, vibrational and rotational part:

\[
|\psi^+\rangle = |\psi_{E^+}^+ \psi_{V^+} \psi_{R^+}\rangle ,
\]  (3-5)
where \( E, V, \) and \( R \) stand for the complete set of electronic, vibrational, and rotational quantum numbers respectively. Thus, the dipole matrix element becomes

\[
D (\psi^+ \rightarrow \psi') = \left\langle \psi_E' \psi_V' \psi_R' \mid d \mid \psi_E^+ \psi_V^+ \psi_R^+ \right\rangle.
\] (3-6)

Again the dipole operator can be written as a sum of an electronic part \( d_{el} \) and a nuclear part \( d_{nuc} \). Because \( d_{nuc} \) is independent of the electronic coordinates, and since the electronic states are orthogonal, only the electronic part of the dipole operator need be considered in an electronic transition. The transition matrix now readily factors into two terms [30], so:

\[
|D (\psi^+ \rightarrow \psi')|^2 = \left| \left\langle \psi_E' \psi_V' \mid d_{el} \mid \psi_E^+ \psi_V^+ \right\rangle \right|^2 S_{J^+ \rightarrow J'}.
\] (3-7)

where \( S_{J^+ \rightarrow J'} \) is the rotational line strength factor, otherwise called the Hönl-London factor [12]. The \((2J + 1)\) degeneracy in the initial level, along with substitution of the expression for the transition matrix, reduces the expression for the Einstein \( A \) coefficient to [30, 37]

\[
A_{exc \rightarrow gr} = \frac{64 \pi \nu^3}{3hc^3} \left| \left\langle \psi_E' \psi_V' \mid d_{el} \mid \psi_E^+ \psi_V^+ \right\rangle \right|^2 \cdot S_{J^+ \rightarrow J'} \cdot \frac{1}{(2J^+ + 1)}.
\] (3-8)

For the example of using rotationally resolved \( \text{N}_2^+ (B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+) \) fluorescence intensities to determine the \( B \) state ionic populations, both the ionic states belong to Hund's case (b) [12]. Since the spin vector \( (S = 1/2) \) is very weakly coupled to the projection of the total orbital angular momentum along the internuclear axis \( (\Lambda = 0) \),
the separation of sublevels with \( J = N + 1/2 \) and \( J = N - 1/2 \) for a given total orbital angular momentum, \( N \), is very small compared to the separation between successive rotational levels. The rotational levels can then be labeled by \( N \), and so we can rewrite the intensity expression as

\[
I_{N^+ \rightarrow N'} = n_{N^+} \cdot \frac{64 \pi |\langle \psi_E^+ \psi_{\nu'} | d_a | \psi_E^+ \psi_{\nu'}^+ \rangle|^2}{3hc^3} \cdot \frac{S_{N^+ \rightarrow N'} \cdot \nu^3}{(2N^+ + 1)}. \quad (3-9)
\]

Substituting the H"{o}nl-London factors for the R-branch (\( \Delta N = N' - N = +1 \)) and the P-branch (\( \Delta N = -1 \)) transitions [12], the rotational populations are estimated using:

\[
n_{N^+} = K \cdot I_{N^+ N'} \cdot \frac{2N^+ + 1}{N^+} \cdot \nu^{-3} \quad \text{for R-branch transitions}, \quad (3-10a)
\]

\[
n_{N^+} = K \cdot I_{N^+ N'} \cdot \frac{2N^+ + 1}{N^+ + 1} \cdot \nu^{-3} \quad \text{for P-branch transitions}. \quad (3-10b)
\]

When generating rotational branching ratios, the constant factors contained in ‘\( K \)’ drop out, and thus the relative rotational populations following photoionization can be determined.

3.2 Experimental scheme

The overall experimental setup involves bringing together the three aspects involved in such gas-phase photoionization studies. It requires channeling the ionizing radiation to the region where the gas sample is prepared, and detecting any fluorescence coming from the interaction region. A detailed view of the experimental setup is pictured in Fig. 3.2. Monochromatized light (\( h\nu_{\text{exc}} \)) is allowed
to interact with a cooled gas phase sample, prepared by supersonic free-jet expansion. Fluorescence is collected from the interaction region by a collimating lens, $L_1$, and is focused onto the entrance slit of a monochromator by a second lens, $L_2$. The dispersed fluorescence intensity is then measured either by a cooled photomultiplier tube or by a CCD multichannel analyzer. The Aluminum photodiode and Tungsten mesh are used for monitoring the intensity of ionizing radiation incident on the gas sample. Fluorescence spectra are thus taken for different excitation energies, which allows us to look at the dynamics of photoionization. Let us now discuss separately each of the mentioned aspect of the experiment.

![Schematic of the experimental layout.](image)

**Figure 3.2: Schematic of the experimental layout.**

### 3.2.1 Tunable light source: synchrotron radiation

One of the most desirable properties of a light source for comprehensive studies of ionization dynamics is tunability. Synchrotron radiation emitted by accelerated electrons (or positrons) is indeed the only effective source of photons in
the energy range of 20-1000 eV [2]. We have used synchrotron radiation produced
from the 1.3 GeV electron storage ring at the Center for Advanced Microstructures
and Devices (CAMD) facility [41] for the purposes of the ionization studies
described here.

The continuous spectral output of the storage ring is monochromatized by a
6 m plane grating monochromator (PGM) [42]. This versatile beamline was designed
to be operated in a variety of modes. Figure 3.3 is a schematic, showing two of the
optical elements in the grating chamber, indicating two possible positions of a
translatable and rotatable premirror.

![Grating and Pre-mirror](image)

Figure 3.3: Motion of the pre-mirror used to accommodate working at different
angles of incidence on the grating, at the PGM beamline in CAMD.

By making the motion of this pre-mirror independent of the rotation of the grating,
the angle of incidence on the grating can be varied for operating in different modes.
For example, in the high throughput mode, the pre-mirror is set so that the grating is
always on blaze. During our measurements, the grating was predominantly operated
in the high throughput mode, except when the excitation energies were below 50
eV, where higher order effects are significant [43]. At these energies, the higher
order rejection mode of operation is preferred. The exact pre-mirror angles used for
various energy ranges is listed in Appendix A. Another important aspect to the
beamline is its energy calibration, which was accomplished by photoelectron measurements, the results of which are listed in Appendix B for future reference purposes. This is particularly important when operating at high photon energies, because the offset has been found to be as large as 12 eV at an apparent photon energy of 200 eV. The beamline was operated with slit widths \( \approx 1 \text{mm} \) corresponding to an excitation band width \( \approx 0.5 \text{ eV} \) at \( h\nu_{\text{exc}} \approx 20 \text{ eV} \).

### 3.2.2 Molecular Beams

We use supersonic free-jet expansion to prepare the gas sample for our photoionization studies. This molecular beam technique has been examined in great detail and is a separate field in its own right [44]. Only its salient features will be addressed here. It involves allowing the gas to expand through a narrow orifice, across a pressure gradient sufficient to provide the gas supersonic flow speeds. The supersonic expansion of the gas and the subsequent redistribution of its internal energy results in cooling of the gas without condensation. This molecular beam is directed such that the gas intersects the path of the incident radiation, and so we now have an isolated gas sample (absent a gas cell whose walls can absorb good part of the incident radiation and fluorescence), with its rotational and vibrational degrees of freedom cooled to very low temperatures. Cooling the gas has the advantage of limiting the number of initial states available for photoionization, which not only reduces the complications involved with interpreting spectra but also aids detection by concentrating the transition strengths to narrow spectral regions.

The sample gasses (N\(_2\) and CO) are allowed to expand through a 50 \( \mu \text{m} \) orifice into the chamber maintained between 1 to 8 times \( 10^{-4} \) torr. The gas pressure behind the orifice, i.e. the stagnation pressure, is set between 2.1 to 16 atmospheres, depending on the sample density or cooling wanted in the interaction region. Cooling achieved is a critical function also of the distance from the nozzle;
collisional redistribution of the internal energies between various degrees of freedom continues taking place till the sample density drops so low that no more cooling takes place. The gas-jet orifice was positioned so that the distance of the interaction region from the orifice was 5mm down stream. With the above conditions, rotational temperatures as low as 18 K have been achieved. Note that condensation does not occur because the densities are not large enough to allow three-body collisions needed for a gas to condense.

3.2.3 Dispersed Fluorescence

Figure 3.2 illustrates the essentials of the optics involved in collecting, dispersing and detecting fluorescence from the interaction region. It is collected by a 100 mm focal length plano-convex lens (L1), that is positioned so that its focus lies within the interaction region. A 100 mm focal length concave mirror is placed 20 cm below the interaction to reflect any fluorescence to the collimating lens and so double the collection efficiency. A plane mirror then reflects the collimated beam onto another plano-convex lens L₂ (focal length \( f = 125 \) mm), which focuses the light into the entrance slit of an optical monochromator (Instruments SA, Model HR 640). The focal length of L₂ was chosen so as to match the \( f \)-number of the dispersing monochromator (\( = 5.2 \)) [44]. The focal length of L₁ was chosen so as to balance the conflicting requirements of efficient light collection (short focal length) and minimizing aberrations (a focal length matching that of L₂) and reducing scattered light (long focal length) [44]. For additional flexibility to fine-tune the focusing onto the monochromator entrance slit, the lens L₂ is mounted on an XY-positioner. Then finally, light dispersed by the optical monochromator is focused onto an optical multichannel detector. The dispersion of the monochromator is determined by the grating used. For the vibrationally-resolved measurements on N₂ and CO, a grating with 1200 grooves/mm (reciprocal linear dispersion = 12 Å/mm)
was used, while for the rotationally-resolved spectra, a grating with 3600 grooves/mm (reciprocal linear dispersion = 4 Å/mm) was found suitable. For example with N₂, working slit widths of 1.5mm (grating-1200 grooves/mm) and 0.15mm (grating-3600 grooves/mm) provide bandwidths of 18 Å and 0.6 Å for vibrational and rotational resolution, respectively.

3.2.4 Optical Multichannel Analyzer

Fluorescence spectra are obtained using a multichannel analyzer as opposed to a single-channel photomultiplier detector. A 256 x 1024 array charge coupled device (CCD) detector (Princeton Instruments # LN/CCD-1024-EUV) with an active area of 25mm x 6.25mm, was employed for the purposes of photon counting. Such a multichannel detector can be thought of as a two dimensional grid of photon detectors (pixels), each of which senses the intensity of light falling on its collection area. Then, as illustrated in Fig. 3.4, the intensities of pixels perpendicular to the direction of dispersion are summed to give the intensity of a spectral line. The

![13 x 3 array CCD](image)

Figure 3.4: Illustration of the data taking method for spectroscopy purposes using a CCD. The intensity displayed is the vertically summed number of events in each pixel.
advantage over single-channel detectors is that fluorescence intensities are measured simultaneously over the entire spectral range of interest, thereby greatly reducing the data taking time [3]. An additional advantage, when the intention is to generate branching ratios from fluorescence intensities, is that the spectra are obtained when the fluorescing sample is under identical excitation conditions. This eliminates any uncertainties introduced because of changing excitation photon flux.

A charge-coupled device is essentially a shift register formed by an array of closely spaced Metal-Oxide-Semiconductor (MOS) capacitors [46] that functions as a device that converts optical images to electronic outputs [47]. The CCD performs two functions, namely, converting photons to electrical charge and moving around this charge to be read out. These functions are carried out in two successive steps: in the first period the photodiodes are exposed to light and in the latter period the stored charge is read out. The length of the first period, during which an external shutter is kept open, is referred to as the exposure time, while the length of the second period is the readout time, during which time the shutter is closed. The CCD detector is a very sturdy detector that is able to handle a wide range of light intensity levels.

A CCD type multichannel analyzer does come with its own drawbacks [47]. Cosmic-ray induced artifacts are a major source of contamination in spectra requiring long exposure times, as when fluorescence signals are weak. Cosmic-ray counts are seen as narrow spikes in the data and occur randomly over the detector area. The underlying experimental data is usually slowly varying as opposed to cosmic-ray induced spikes that have amplitudes of the order of thousands of counts and are no more than 5 pixels wide. This occurrence is used to detect and delete any cosmic-ray spikes in the spectra. Typically, the spikes are replaced by interpolated data, so as to be able to preserve as much of the original data as possible. A practical
limitation resulting from cosmic-ray contamination is that exposure times can be no
longer than approximately 300s for a detector of the size used here. All the same,
cosmic-ray spikes were not a serious impediment in the current work, partly because
the regions of interest in each snap-shot of the CCD image typically covered a small
area, and consequently there were very few spectra with cosmic-ray contamination
within the regions of interest.

There are two other error considerations that have to be taken into account
in a CCD type detector. They are the readout noise and dark charge counts [47]
that have to estimated for calculations of uncertainties in the spectral intensities (i.e.,
signal-to-noise ratios). Readout noise, as its name suggests, is the noise associated
with each readout of the data from the shift registers. It is independent of the
collection (exposure) time and depends primarily on the number of readout steps
required for digitizing an image. Dark charge counts, however, depend on the
exposure time as they are counts from the thermally generated charges. Hardware
binning, i.e. adding multiple pixels together as though they were one larger pixel can
improve the signal-to-noise ratio with respect to the readout noise. The dark charge
counts are exponentially temperature dependent, hence lowering the detector
temperature can reduce dark charge counts dramatically.

The scatter purely from readout noise is estimated by reading out empty
pixels. This is typically done by ‘counting’ for zero time, so that the scatter in the
data is only from reading out the empty pixels. The dark charge is estimated by
collecting data with no light falling on the CCD, and the counts subsequently used in
the data analysis. The signal counts, generated by optical photons, during a certain
time period, is described by the Poisson probability distribution. The thermal
generation of electron-hole pairs is similar to the optical generation and is also
described by a Poisson distribution. Consequently it can be clubbed together with the
general background noise from light scattered within the monochromator. The readout noise, as mentioned earlier, is constant for a given data taking setup and has to be treated separately. The relative uncertainty in the net signal can now be estimated as follows:

\[
\frac{\Delta S_{\text{net}}}{S_{\text{net}}} = \sqrt{\frac{(S_{\text{tot}} - S_{\text{read\,out}}) + S_{\text{back}} + (\Delta S_{\text{read\,out}})^2}{(S_{\text{tot}} - S_{\text{read\,out}}) - S_{\text{back}}}},
\]  

(3-11)

where the net signal \(S_{\text{net}}\) is the result of subtracting the background signal \(S_{\text{back}}\) and the readout noise \(S_{\text{read\,out}}\) from the total signal \(S_{\text{tot}}\). The background signal here includes the aforementioned background scatter and dark charge counts. It should be noted that the detector has a bias level of nearly 100 counts that is simply subtracted from the spectra.

3.2.5 Vacuum Considerations

Gas phase experiments with synchrotron radiation are complicated by the stringent vacuum requirements of beamlines and storage rings. The need to maintain and protect the ultra-high vacuum (UHV) requires that the sample chamber be isolated from the beamline and yet be transparent to the radiation of interest. There are two ways of tackling this problem: by the use of differential pumping or by the use of thin filters, and we shall outline the use of both techniques.

The two-stage differentially pumped setup essentially involves the use of two capillary tubes of 2mm internal diameter (ID) to channel the radiation to the interaction region, and yet the combined conductance of the two tubes is kept so low that the vacuum integrity of the beamline is maintained [48]. As described schematically in Fig. 3.5, the region between the two capillaries is also pumped on so as to provide a high conductance path for the gas molecules that flow through the
first stage capillary connected to the interaction region. The result is that the intermediate chamber that is connected to the beamline is able to maintain UHV conditions when the experimental chamber pressures are as high as $10^{-3}$ torr.

![Diagram](image)

**Fig. 3.5** Schematic of the differential pumping setup used for maintaining the vacuum integrity of the beamline.

The minute, yet finite, throughput of the differential pumping technique can be a disadvantage when dealing with gases that can damage beamline optical elements when present even in small amounts. Another technique is used under such circumstances, involving the use of thin film filters to isolate the experimental chamber from the beamline [49]. The transmission characteristics of the filter material is chosen such that it transmits that wavelength region of the synchrotron radiation that is of interest to the experimentalist. We employed a custom-made compact UHV-compatible gate valve (VAT 01032-UE01-X) with replaceable Aluminum filter windows (Luxel VF111-a), typically 1500 Å thick. A minor constraint in the setup was the need to insert an adapter piece (a bellows) between the beamline gate valve and the filter-mounted gate valve. This was because gate valves have internal threads and so cannot be bolted to one another. The issue here is that when both gate valves are closed, the in-between volume is not being pumped
Consequently, a careful yet simple “common-sense” procedure was followed for opening up to the beamline. Another important precaution to be taken regarding the use of filters is to check the compatibility of the filter material with the gas sample and with the products of the interaction of synchrotron radiation with the gas. Even a small amount of reactivity can eat away at a 1500 Å thick filter and vent the corrosive gasses into the beamline.

This completes the discussion of the experimental details. The results obtained using the described procedures are now presented.
CHAPTER 4

RESULTS AND DISCUSSION

The data presented in this chapter deals with the results of studying the iso-electronic molecules, $N_2$ and CO, using the experimental techniques just described. Their ground state electronic configurations can be written as $N_2$-$\{K, K, (2\sigma_g)^2, (2\pi_u)^2, (1\pi_u)^4, (3\sigma_g)^2\}$ and $CO$-$\{K, K, (3\sigma)^2, (4\sigma)^2, (1\pi)^4, (5\sigma)^2\}$. The difference in the labeling of the energy levels comes from the absence of inversion symmetry in CO [12]. We will see that the presence or absence of inversion symmetry makes an enormous difference in the allowed partial waves of the continuum electron (see Eqs. (2-14) and (2-15)), and ultimately in the dynamics of photoionization.

4.1 Vibrationally Resolved $N_2$ 2$su^{-1}$ Photoionization

There have been a number of vibrationally-resolved photoionization studies of $N_2$ that have been largely confined to photon energy ranges where autoionizing transitions or shape resonances exist [7, 27, 50]. Motivated to study channel coupling effects, fluorescence spectroscopy measurements of the $2\sigma_u \rightarrow k\sigma_g$ ionization channel were again confined to that photon energy range where autoionization or shape resonance effects dominated, namely threshold to 40 eV [48, 51, 52]. The study described in this dissertation truly exploits the tunability of synchrotron radiation sources; the results of a survey of the ionization continuum, by measuring vibrational branching ratios, is now discussed.
Figure 4.1: Fluorescence spectrum from N$_2$\(^+\) showing \(v'' = v^+ + 1\) transitions of \(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+\).

Relative ionization rates to the \(v^+ = 0, 1,\) and 2 vibrational levels of N$_2^+ (B^2\Sigma_u^+)$ state are determined by monitoring the dispersed \((B^2\Sigma_u^+,v^+ \rightarrow X^2\Sigma_g^+,v'' = v^+ + 1)\) fluorescence. Shown in Fig. 4.1 is a portion of the mentioned fluorescence spectrum including the transitions originating from the \(v^+ = 0, 1,\) and 2 levels. The spectra were collected with the fluorescence bandwidth adjusted to \(\Delta \lambda \approx 15\ \text{Å},\) sufficient for vibrational resolution. Such spectra are generated for photon energies \(25 \leq h\nu_{\text{exc}} \leq 250\ \text{eV}\) and subsequently used to determine the vibrational branching ratios.
4.1.1 Franck-Condon breakdown from Cooper minima

The vibrational branching ratios are derived from fluorescence intensity ratios using Eq. (3-4). Shown in the bottom frame of Fig. 4.2 are the so-derived $v^+=1/ v^+=0$ branching ratios, plotted as a function of photon energy. The top frame serves to put the current work in context and shows the PES generated branching ratios for the $N_2 3\sigma_g^{-1}$ channel (shown earlier in Fig. 2.5), now plotted to the energy scale of the $2\sigma_u^{-1}$ results.

![Graph showing vibrational branching ratios](image)

Figure 4.2: Top frame: $3\sigma_g^{-1}$ vibrational branching ratio results shown previously in Fig. 2.5 now drawn to the energy scale of the new results in the bottom frame.

Bottom frame: $2\sigma_u^{-1}$ vibrational branching ratios obtained from dispersed fluorescence measurements.
This comparison serves to emphasize the broad range of the observed Franck-Condon breakdown (or vibrational-electronic coupling), which dwarfs the features of the usually-considered broad shape resonance induced curve. The curves plotted in Fig. 4.3 show the complete results of the measured vibrational branching ratios for $v^+=1/ v^+=0$ and the much weaker $v^+=2/ v^+=0$ channel. The deviations from Franck-Condon behavior are clearly observed in the $v^+=1/ v^+=0$ ratio but are even more evident in the weaker $v^+=2$ channel. It must be emphasized here that while the absolute partial cross sections do not deviate substantially from Franck-Condon predictions, the branching ratios (which emphasize their relative magnitudes) highlight the deviations clearly.

Another empirical characteristic of the FC breakdown is the spectral width of the feature. The broad peak in both frames of Fig. 4.3 reflects deviations from Franck-Condon behavior that set in at $h\nu_{exc} \approx 100$ eV and persist up to 200 eV, showing that molecular aspects of the process set in and last beyond 80 eV above the ionization threshold. Also, the branching ratios change gradually so that tests for the validity of the FC approximation that rest on measurements of vibrational intensities at energies separated by a few eV can be misleading. Theoretical predictions of the $v^+=1/ v^+=0$ branching ratio agree very well with experiment while there is only qualitative agreement between them for the $v^+=2/ v^+=0$ branching ratios. All the same, we shall see the crucial role that theory plays in interpreting these results and this is bound to be so particularly in those cases when experiments cannot be performed over such large excitation energy ranges.

Recent rotationally-resolved measurements have hinted at the possible reason for the observed Franck-Condon breakdown [31,34]. It was seen that rotational...
Figure 4.3: $2\sigma_u^{-1}$ vibrational branching ratios obtained from dispersed fluorescence measurements.
branching ratios of the $v^+ = 0$ vibrational level, following $2\sigma_u^{-1}$ photoionization, exhibit inflection points at $h\nu_{\text{exc}} \approx 120$ eV. For example, Fig. 4.4 shows the dramatic change in the relative rotational population with increasing photon energy.

Figure 4.4: $N_2^+ (B^2\Sigma_u^+, v^+ = 0)$ rotational populations vs $h\nu_{\text{exc}}$.

Theoretical calculations showed that the energy dependence of the photoion rotational distributions resulted from Cooper minima in the $\ell=2$ and $\ell=4$ partial waves of the $2\sigma_u \rightarrow k\sigma_g$ ionization continuum (see Fig. 4.5). In other words, the undeniably molecular nature of ionization dynamics of $N_2$ persists deep into the ionization continuum. We know that, in scattering processes, molecular behavior is differentiated from the atomic primarily by its ‘non-zero internuclear separation’. The ensuing step then is to examine the $R$-dependence of these molecular Cooper minima in the $\ell=2$ and $\ell=4$ waves. The calculated dipole strengths at different
internuclear distances for the dominant partial wave components contributing to the $2\sigma_u \rightarrow k\sigma_g$ channel is plotted in Fig. 4.6. The partial waves that go through a Cooper 'zero' show a pronounced shift to lower photon energies with increasing internuclear separation. We already know, from the discussion in relation to Eq. (2-8), that a strong R-dependence of the electronic transition probability (or its dominant components in this case) will result in a breakdown of the Franck-Condon approximation. So we see that the peaks in the vibrational branching ratios of Fig. 4.3 are because of the shifts in the Cooper minima.

![Figure 4.5: Dipole strengths for $N_2 \ 2\sigma_u \rightarrow k\sigma_g$ channel photoionization.](image)

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The empirical arguments made above for explaining the non-FC behavior do not address the basic question of why the Cooper minima are shifting with internuclear separation. From the discussion in section 2.2, we have seen that FC breakdown can be attributed to 'initial' or 'final' state effects. One would then expect Cooper minima effects to be classified as 'initial state' effects. But it should be pointed out right away that this is not necessarily so in molecular systems where 'rescattering', or interaction between the outgoing electron and the remnant photoion, can play a significant role. For a better grip on the arguments we again fall back on the calculations of Wang and McKoy. Their calculation of the ground state wave function of N\textsubscript{2} shows the 2\sigma\textsubscript{u} orbital to have 90.65\% \textit{p}, 6.66\% \textit{f}, and 1.52\% \textit{h} character at the equilibrium internuclear distance of \( R_e = 2.0743 \) a.u. This orbital composition evolves slowly from 98.86\% \textit{p} and 2.62\% \textit{f} at \( R = 1.25 \) a.u. to 81.52\% \textit{p} and 11.30\% \textit{f} at \( R = 3.5 \) a.u. Thus the angular momentum composition of the target state orbital changes gradually with bond length. Ionization to alternative vibrational levels results in different ranges of the internuclear separation to be sampled. As a result any parametric R-dependence of the electronic transition probability will translate to non-FC vibrational distributions. Yet in the case of N\textsubscript{2}, the relatively slow change in the 2\sigma\textsubscript{u} orbital character over the pertinent range of internuclear separation suggests a necessary contribution from 'final state' effects, i.e., from the R-dependence of the rescattering of the continuum electron into partial waves. As mentioned in the discussion in section 2.2.1, it is likely that when an overall partial wave contribution falls because of a Cooper zero, the 'minor' contributing factors to those channels, like the 'final state' effects, get magnified. All in all, it is expected that both effects contribute to the observed R-dependence of the Cooper minima.
Figure 4.6: Dipole strengths for the dominant partial waves of the $N_2$ $2\sigma_u \rightarrow k\sigma_g$ channel. Note the $R$-dependence of the $\ell=2$ and $\ell=4$ partial waves.
4.1.2 Rectification of earlier continuum channel coupling data

A minor digression is necessary here to address what appears to be a disagreement between the $v^+=2/v^+=0$ branching ratio results presented here and those published previously [48, 53]. Earlier fluorescence measurements of the $v^+=2/v^+=0$ branching ratio, over the photon energy range 25 to 55 eV, were scaled incorrectly and so appear to be different from the data reported in Fig. 4.3. In fact the two curves show excellent agreement if the previous data are scaled correctly, as shown in Fig. 4.7. The previous measurements were taken using a single channel detector, [48] which requires that the branching ratios be generated by appropriately

![Graph showing branching ratio vs photon energy](image)

Figure 4.7: The earlier fluorescence measurements corrected and compared to the present results.
scaling the ratios of the fluorescence intensity scans. The scaling factor, derived from earlier erroneous data, resulted in an incorrect evaluation of the absolute value of the branching ratios.

The motivation for the mentioned earlier measurements was to probe continuum channel coupling effects. Specifically, it was to characterize the interchannel effects between the $3\sigma_g^{-1}$ and the $2\sigma_u^{-1}$ channels of the ionization continuum of $N_2$. The $2\sigma_u^{-1}$ channel does not support any shape resonances while the $3\sigma_g^{-1}$ channel shows distinct shape resonance character. Calculations that explicitly include multichannel effects have predicted channel coupling effects, which was the motivation for the earlier study. Clearly, none of the important points made in that study need to be changed or rephrased on account of the scaling error, and yet the correction is important for precise comparisons with calculated or PES generated Franck-Condon factors for ionization to the $N_2^+(B^2\Sigma_u^+)$ state.

4.2 Vibrational-Rotational-Electronic (V-R-E) correlations in $N_2$

$2\sigma_u^{-1}$ Photoionization.

The non-FC effects described earlier are an example of how vibrationally resolved spectra can probe correlations between nuclear vibration and electronic motion. We have therefore seen that Cooper minima can lead to Franck-Condon breakdown over a broad energy range. Measurements of the photoion rotational distributions have already demonstrated the influence of Cooper minima on the angular momentum partitioning between the photoion (rotation) and photoelectron [31, 34]. The subsequent step then would be to compare the photoion rotational distributions of different vibrational levels. Such measurements not only access the underlying dynamics of the coupling between electronic and nuclear motion, but also, for the first time, combine vibrational and rotational studies for investigation of
correlations between vibrational, rotational, and electronic motions (V-R-E correlations) over a broad electron energy range.

To compare the photoion rotational distributions of $v^+=0$ to that of $v^+=1$, we detect rotationally resolved fluorescence from both vibrational levels simultaneously. Shown in Fig. 4.8 is one such snap shot of rotationally resolved spectra that are taken over the energy range $25 \leq h\nu_{\text{exc}} \leq 210$ eV.

![Fluorescence spectrum](image)

Figure 4.8: Rotationally resolved fluorescence spectrum showing the $v^+=0 \rightarrow v''=1$ and $v^+=1 \rightarrow v''=2$ vibrational transitions.

The rotational populations are then extracted from fluorescence intensities using Eq. (3-10a) and (3-10b) and are normalized to within the vibrational branch. The so extracted rotational branching ratios of $v^+=0$ and $v^+=1$ levels are plotted in Fig. 4.9

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as a function of the excitation photon energy. The results show right away the different trends in the relative rotational populations of the different vibrational levels.

\[ \text{N}_2^+ (B^2\Sigma_u^+) \]

- Vibrational level \( v^+ = 0 \)
- Vibrational level \( v^+ = 1 \)

Figure 4.9: Comparison of relative rotational populations for \( v^+ = 0 \) and \( v^+ = 1 \) vibrational levels from spectra such as those shown in Fig. 4.8.

The theoretical curves are plotted along with the experimentally determined rotational populations in Fig. 4.10. The agreement between theory and experiment is excellent, so we can examine the experimentally measured trends in the rotational populations together with the theoretically predicted curves. In the lower rotational levels (\( N^+ = 1 \) and 2), both experiment and theory show a consistently higher
population for the $v^+=0$ level than for the $v^+=1$ vibrational level. On the other hand, the higher rotational levels ($N^+ = 4$ and 5) show a lower population for $v^+=0$ than

![Diagram](image)

Figure 4.10: Experimental and theoretical values of the relative rotational populations of $N_2^+ (B^2\Sigma_u^+)$ state $v^+=0$ and $v^+=1$ vibrational levels.

for the $v^+=1$ vibrational level. The intermediate nature of the $N^+ = 3$ rotational level is reflected in both theory and experiment, where the $v^+=0$ population is slightly lower at photon energies below 175 eV and overtakes that of the $v^+=1$ at higher photon energies. There is a significant discrepancy between the calculated and
measured \( N^+ = 4 \) population for the \( v^+ = 1 \) level. We are yet to determine the origin of this discrepancy.

A closer look at the results in Fig. 4.10 reveals a pattern to the differences in the rotational populations for \( v^+ = 0 \) versus \( v^+ = 1 \). Starting with the similarities first, the rotational distributions in both vibrational levels change dramatically with photon energy, with the populations of lower rotational levels decreasing and those of higher rotational levels increasing. This implies that larger \( \Delta N \) ionizing transitions increase with photon energy, as seen previously for \( v^+ = 0 \) [10]. Such is the case in the rotational distributions following ionization to the \( v^+ = 1 \) vibrational level too, where low \( \Delta N \) transitions (i.e., \( \Delta N = \pm 1 \)) dominate at lower photon energies, while larger \( \Delta N \) transitions (i.e., \( |\Delta N| \leq 3 \)) grow in importance as the photon energy is increased. This overall trend is accelerated at the inflection point at 120 eV. Thus the two rotational populations largely track one another from the ionization threshold up to \( h\nu_{\text{exc}} \approx 100 \) eV. It is beyond this photon energy that stark differences in the ion rotational populations are seen for these two vibrational levels. Consider for example the \( N^+ = 1 \) and \( N^+ = 5 \) rotational populations highlighted in Fig. 4.11. The inflection point in the relative rotational populations is shifted down to \( h\nu_{\text{exc}} \approx 100 \) eV for \( v^+ = 1 \), from \( h\nu_{\text{exc}} \approx 120 \) eV for \( v^+ = 0 \). In other words, larger \( \Delta N \) transitions are setting in at lower photon energies for the \( v^+ = 1 \) vibrational level than that for \( v^+ = 0 \).

We clearly have a vibrational state dependence in the partitioning of angular momentum between the photoelectron and ion core.

To interpret the dynamics of the ionization process, we shall once again examine the \( R \)-dependence of the partial wave compositions of the photoelectron matrix element (see Fig. 4.6). Of the dominant partial waves, only the \( \ell = 2 \) and \( \ell = 4 \)
Figure 4.11: Comparison of two relative rotational populations for \( v^+ = 0 \) and \( v^+ = 1 \).
curves show a dramatic dependence on the internuclear separation. Taking the cue from the vibrationally-resolved results that demonstrated that the effects of R-dependent Cooper minima, we now examine the partial wave composition of the photoelectron matrix elements vibrationally averaged over the appropriate range of internuclear separation, plotted in Fig. 4.12. The R-dependence of the angular momentum partitioning is apparent, and this shift of Cooper minima to lower energies results in the suppression of high-\ell components at a lower photon energy on ionization to the \( v^+ = 1 \) vibrational level than for \( v^+ = 0 \). Subsequently, the
enhancement of the $\ell=2$ and $\ell=4$ components at higher energies results in large $\Delta N$ transitions dominating earlier in the photoionization to $v'^+=1$ than $v'^+=0$.

In conclusion, we have looked at the underlying dynamics involved in the non-Franck-Condon effects caused by Cooper minima by comparing the finer rotational structure in different vibrational states. The expectation is still that both 'initial' and 'final' state effects could contribute to the $R$-dependent behavior of the Cooper minima.

4.3 Vibrationally Resolved $4\sigma \rightarrow 1 \pi$ Photoionization of CO

This study of CO photoionization was motivated by the earlier rotationally resolved measurements that indicated the presence of an intense shape resonance in the $4\sigma \rightarrow k\sigma$ continuum [48, 54]. The resonance region covered the photon energy range from 30 to 50 eV and there is no counterpart to the Cooper minimum seen in N$_2$. With no mechanism to couple the vibrational and electronic degrees of motion above photon energies $\sim$ 50 eV, the branching ratios are expected to be independent of the electron ejection energy for $E_k \geq 35$ eV.

The excitation and fluorescence sequence used for vibrationally resolved measurements is:

$$\text{CO} \left( X^1\Sigma^+, v = 0 \right) + h\nu_{\text{exc}} \rightarrow \text{CO}^+ \left( B^1\Sigma^+, v'^+ \right) + e^-$$

$$\downarrow$$

$$\text{CO}^+ \left( X^2\Sigma^+, v'' \right) + h\nu_{v'^+ v''} . \quad (4-1)$$

The relative ionization rates to alternative vibrational levels are determined by monitoring vibrationally-resolved fluorescence intensities, as was done for N$_2$. A typical vibrationally-resolved fluorescence spectrum is displayed in Fig. 4.13, where fluorescence transitions originating from the $v'^+ = 0, 1, 2,$ and $3$ are monitored. The
Figure 4.13: Vibrationally-resolved fluorescence spectrum showing $v'' = v^+ + 2$ transitions.

Intensity ratios are then used to generate vibrational branching ratios using Eq. (3-4). The results are plotted in Fig. 4.14 and show their non-FC behavior below $h\nu_{\text{exc}} \approx 50$ eV. These features are discussed in detail elsewhere [48] and will not be addressed here. Instead, the point of discussion is the lack of features in the $v^+ = 0$, 1, and 2 vibrational branching ratios, above an excitation energy of 50 eV. These ratios that are constant above 50 eV serve to contrast the results of N$_2$ vibrational branching ratios. However, the non-FC behavior of the $v^+=3/v^+=0$ branching ratio even above 50 eV stands out. It is expected that the reason for the non-FC behavior of $v^+=3$ channel is because it samples that range of internuclear separation where the parametric dependence starts to show.
Figure 4.14: Vibrational branching ratios for CO $4\sigma^{-1}$ photoionization.
4.4 K-shell Photoionization of N\textsubscript{2}

We have seen the advantages of employing dispersed fluorescence spectroscopy for high resolution photoionization studies as applied to valence electron ionization. However, applying the same for core-electron ejection is greatly complicated by the many alternative decay pathways available to a core-hole state. For example, in N\textsubscript{2}, the dominant process following the absorption of a soft x-ray photon is fragmentation [55]. Yet, there is great interest in studying the fewer unfragmented molecules / ions because they carry the molecular characteristics of vibrations and rotations that are sensitive probes of the state formed following the absorption of a soft x-ray photon. In the case of N\textsubscript{2}, probing vibrational motion of molecular ions can be effective for studying shape resonances known to exist in the ionization of the 1s core electron [8]. However, vibrationally-resolved data on core electron ionization have been inaccessible, owing to lifetime broadening and instrumental resolving power limitations [56]. In other words, it makes an attractive system to apply the technique of detecting dispersed fluorescence.

The decay of photo-excited core-hole states of N\textsubscript{2} are probed by monitoring the \((B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)\) fluorescence. By vibrationally resolving this fluorescence, we can now monitor the coupling of the vibrational levels of the 1s\textsuperscript{-1} state to that of the 2\sigma_u\textsuperscript{-1} state. Figure 4.15 is a schematic of the process that is studied by this method of monitoring the \(B \rightarrow X\) fluorescence following soft x-ray absorption. The two distinct species thus created, the core-hole ion (N\textsubscript{2}\textsuperscript{+}; 1s\textsuperscript{-1}) and the core-hole excited state (N\textsubscript{2}; 1s\textsuperscript{-1}, 1\pi_g), will be treated separately for the sake of clarity. Let us now take a look at the excitation spectrum generated by tuning through the nitrogen K-edge.
Figure 4.15: Schematic of the excitation and decay sequence for the N\(_2\) system. Decay to the N\(_2^+\) B-state is probed by monitoring the dispersed \(B \rightarrow X\) fluorescence.

Figure 4.16 shows the intensity of fluorescence from different vibrational levels of the N\(_2^+(B^2\Sigma_u^+)\) state in the region of the nitrogen K-edge. A comparison with the “pseudophoton” absorption spectrum [8, 10], plotted in Fig. 4.17, shows that the pre-edge core-hole resonance, and the double excitations and shape resonance above the K-edge, are clearly present. There is also more structure in the \(v'=2\) excitation spectrum than can be accounted for by the “pseudophoton” absorption spectrum [10]. A quick comparison of the vibrational branching ratios
with that at non-resonant energies, given in Table 3.1, indicate a difference, thereby leaving a lot that has to be looked into.

Figure 4.16: Vibrationally-resolved fluorescence excitation spectra in the region of the nitrogen K-edge. The peak below the K-edge ionization threshold at $h\nu \approx 401$eV is due to the $1s \rightarrow 1\pi_g$ transition.
Figure 4.17: Comparison of the “pseudophoton” absorption spectrum (line - reference [10]) with the $B \rightarrow X$ dispersed fluorescence excitation spectrum (error bars) originating from the $v'=2$ vibrational level of the $B$-state.

The theoretical expectations of the resulting branching ratios after excitation through the vibrational manifold of the neutral core-hole state (pre-edge structure) can be estimated as follows (see Fig. 4.18) [57, 58, 59, 60]:

$$
\sigma_{v',\nu}(h\nu_{\text{exc}}) \propto \left| \sum_n \frac{\langle v' | n \rangle \langle n | 0 \rangle}{h\nu_{\text{exc}} - (E_n - i \Gamma / 2)} \right|^2.
$$

(4-2)

The branching ratio derived using the above equation gives a value $\sigma_1/\sigma_0 = 0.76$, where the relevant vibrational wavefunctions were generated using Morse potentials [61]. This value is dramatically different from the experimentally observed values listed in Table 3.1.
Figure 4.18: Schematic representation of the coherent excitation of the lifetime broadened vibrational levels \( (E_n) \) of the intermediate state. \( E_0 \) represents the vibrational ground state of the initial state and \( E_{\nu'} \) the final state vibrational levels.

A variety of factors can contribute to the large difference in vibrational branching ratios \([60]\). Contribution from non-resonant photoionization of the \( 2\sigma_u \) electron has been shown to be insufficient to bridge the gap between the observed and calculated vibrational branching ratios \([60]\).

<table>
<thead>
<tr>
<th>( h\nu_{\text{exc}} ) (eV)</th>
<th>( \sigma_1 / \sigma_0 )</th>
<th>( \sigma_2 / \sigma_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Franck-Condon limit</td>
<td>0.129</td>
<td>0.0026</td>
</tr>
<tr>
<td>50</td>
<td>0.124</td>
<td>0.0032</td>
</tr>
<tr>
<td>401</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>420</td>
<td>0.25</td>
<td>0.06</td>
</tr>
</tbody>
</table>
One contributing factor could be that there are alternative pathways that connect the core-hole neutral and the $B$-state. Information from deexcitation electron spectroscopy (DES) indicates that among the states that $N_2^* \Pi g(1s^{-1}, 1\pi_g)$ can decay to, two states are allowed in principle to decay to the $2\sigma_u^{-1}$ state via a single electron transition. Their electronic configurations are $N_2^+ (D^2\Sigma g^+; 2\sigma_u^{-1}, 1\pi_u^{-1}, 1\pi_g)$ and $N_2^+ (2\Pi g; 2\sigma_u^{-2}, 1\pi_g)$, with 29.4 and 33.2 eV binding energies each [62]. Thus, it is possible that there is contribution to the $B$-state population through autoionization of $N_2^* \Pi g \rightarrow N_2^+ (D^2\Sigma g^+)$ or $N_2^+ (2\Pi g)$. Studies of these two-hole one-electron states have indicated that they are highly dissociative and so the contribution from these alternative paths may not be able to account for the differences in the observed and calculated branching ratios [62, 63]. It is distinctly possible, though, that some additional input is required of the theoretical formulation. Since the equilibrium internuclear separation of the core-hole neutral ($R_e \approx 1.164 \text{ Å}$) is significantly displaced from that of the $B$-state ($R_e \approx 1.075 \text{ Å}$), and the lifetime of the intermediate state is comparable to the time scale of its vibrations [64], a time-dependent formulation may be necessary for accurately portraying the decay of the core-hole state [65].

The decay of the core-hole ion $N_2^+ (1s^{-1})$ can be, in principle, coupled to the $B$-state via the two-hole one-electron states described above. Yet, for the very same reason, that these states have been found to highly dissociative, it is not expected that there is any significant contribution from such alternative pathways. A dominant mechanism populating the $B$-state can be via continuum channel coupling [56], illustrated in Fig.4.19. Analogous to the interchannel coupling discussed earlier in section 4.1.2, it is expected that, following shape resonant excitation, the enhanced
Excite 1s electron into shape resonance.

Continuum coupling

$1s^{-1} \rightarrow 2\sigma_u^{-1}$

$2\sigma_u^{-1}$ state fluoresces

Figure 4.19: Illustration of the continuum channel coupling process in $N_2$, where the resonance character is transferred from the shape resonant ejection of the 1s electron to the $2\sigma_u^{-1}$ continuum.

The amplitude of the photoelectron wavefunction within the molecular confines results in coupling to the $2\sigma_u^{-1}$ continuum and to the two-hole one-particle states that can decay to the $B$-state. A detailed calculation of channel coupling effects describing the coupling of the $2\sigma_u^{-1}$ and $1s^{-1}$ continua is necessary to sift the reasonable coupling mechanisms from those that are speculative.
CHAPTER 5

CONCLUSION

As a result of probing $N_2^+(2\sigma_u^{-1})$ photoion vibrational distributions, an extremely broad range Franck-Condon breakdown ($\Delta E \approx 100$ eV) has been observed. This behavior is attributed to the R-dependence of Cooper minima, the implication being that this is the first non-resonant mechanism that has been observed to exhibit Franck-Condon breakdown. We observe molecular behavior, namely, vibrational-electronic correlations, deep in the ionization continuum where it is usually assumed to be dominated by atomic-like behavior.

In an attempt to probe the underlying dynamics of the observed Franck-Condon breakdown, we have measured the photoion rotational distributions of alternative vibrational states. The result of measuring the vibrational and rotational energy deposition onto the photoion over a broad range of electron energy is that we have been able to get to the fundamental aspects of the dynamics of coupling between electronic and nuclear motion. The results show clearly that the Cooper minima are R-dependent, as the photoion rotational distributions depend on the photoion vibrational state, once again emphasizing the molecular nature of the scattering process. A unifying theme of these studies is that photoionization opens up many avenues for probing correlations between electronic and nuclear degrees of freedom, and such vibrationally- and rotationally-resolved methods are naturally well-suited for the purpose.
The utility of dispersed fluorescence as a survey tool has been repeatedly stressed throughout this study, and yet cannot be emphasized enough. Combining fluorescence detection with the broad tunability of synchrotron radiation can be a particularly useful complement to traditional photoelectron spectroscopy. The large yet limited number of molecules that fluoresce can be similarly characterized using this technique. For example, HCl is a prime candidate for such investigations, as its partial photoionization cross-sections are known to be strongly modulated by the presence of Cooper minima [66].

The preliminary results from the K-edge studies of N₂ show promise of extending dispersed fluorescence techniques to probe core-electron ionization dynamics. However, with unanswered questions regarding the decay mechanism of core-hole states, fluorescence-photoelectron coincidence experiments are planned, so as to quantify the coupling of valence-hole states to core-hole processes. Such understanding can be turned around to use information from valence-hole states to shed light on core-electron excitation phenomenon.
REFERENCES


APPENDIX A

PARAMETERS FOR HIGH THROUGHPUT MODE

The following premirror angles were used at the PGM beamline for the shown apparent energy ranges (see Appendix B for determining the true energy):

Table A.1

<table>
<thead>
<tr>
<th>Energy (E)</th>
<th>Premirror angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E ≤ 30 eV</td>
<td>77.2</td>
</tr>
<tr>
<td>30 ≤ E ≤ 50 eV</td>
<td>77.5</td>
</tr>
<tr>
<td>50 ≤ E ≤ 70 eV</td>
<td>78</td>
</tr>
<tr>
<td>70 ≤ E ≤ 85 eV</td>
<td>80</td>
</tr>
<tr>
<td>85 ≤ E ≤ 100 eV</td>
<td>81</td>
</tr>
<tr>
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<td>82</td>
</tr>
<tr>
<td>120 ≤ E ≤ 140 eV</td>
<td>83</td>
</tr>
<tr>
<td>140 ≤ E ≤ 155 eV</td>
<td>84</td>
</tr>
<tr>
<td>155 ≤ E ≤ 180 eV</td>
<td>84.2</td>
</tr>
<tr>
<td>180 ≤ E ≤ 195 eV</td>
<td>84.8</td>
</tr>
<tr>
<td>195 ≤ E ≤ 210 eV</td>
<td>85</td>
</tr>
<tr>
<td>210 ≤ E ≤ 220 eV</td>
<td>85.1</td>
</tr>
</tbody>
</table>
APPENDIX B

PHOTON ENERGY CALIBRATION

The true photon energy, (as opposed to the apparent energy displayed by the beamline instruments), was determined using photoemission measurements (UPS) with an ellipsoidal mirror analyzer (EMA) [67]. The data was fitted to a quadratic using the least squares method.

\[
Y = 4.32 \times 10^{-4} \times X^2 + 0.9797 \times X + 0.3087
\]

Figure B.1: Photon energy calibration for the PGM beamline at CAMD
VITA

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