Fluorescence Accompanying Photoionization in Polyatomic Molecules and the Relationship to Photoelectron Motion: A Global View.

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FLUORESCENCE ACCOMPANYING PHOTOIONIZATION IN POLYATOMIC MOLECULES AND THE RELATIONSHIP TO PHOTOELECTRON MOTION: A GLOBAL VIEW

A Dissertation

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Louisiana State University and
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by

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Abstract

Measurements of dispersed fluorescence from electronically excited photoions are used to study fundamental molecular scattering phenomena. Our experimental advances make it possible to obtain vibrationally resolved data that offer qualitative insights into photoionization dynamics in polyatomics. In particular, vibrationally resolved data are measured to probe the correlation of electronic and nuclear degrees of freedom via studying the vibrational distributions of photoions and ionic fragments. Vibrational branching ratios are mapped out over an extremely broad energy range (3 ≤ E_k ≤ 200 eV) for N_2O (7σ-1) ionization channel. The origin of the non-Franck-Condon behavior is tentatively interpreted as shape resonances and Cooper minima. The alternative vibrational mode, the bending degree of freedom, is studied for two isoelectronic molecules N_2O and CO_2. The results reveal very interesting information about the trapping site of shape resonant photoionization in a polyatomic molecule: bending motion may change the width of the "box" which traps the photoelectron. The multichannel aspect of shape resonances reflected in continuum channel coupling is investigated for CO_2 (3σ_u-1) channel. Current results are in very good agreements with calculations by Lucchese and McKoy. The dispersed fluorescence spectra of the fragments N_2^+(B^2Σ_u^+, v^+ =0) following dissociative photoionization of N_2O are measured in 20 ≤ hν_{exc} ≤150 eV. Characteristic features observed in the excitation spectrum of N_2^+(B^2Σ_u^+) are discussed with a focus on (pre)dissociation of (1) singly ionized parent states;
(2) multielectron excitation states commonly observed in the inner-valence regions; (3) doubly ionized parent states. The multielectron excitation states and doubly ionized parent states are responsible for most of the dissociative ionization that occurs in N₂O above ~ 22 eV. Strongly dissociative nature of doubly ionized states correlating with the single-hole 4σ shape resonance in inner-valence region is probably responsible for the broad enhancement observed in the CIS curve. The dispersed fluorescence provides information about the internal energy distributions of the fragments and, as a consequence, leads to insights into the dissociation dynamics.
Chapter 1

Introduction

This dissertation focuses on a central theme in chemical physics, the correlation of electronic and nuclear degrees of freedom. Specifically, I describe a program of research into the influence of the photoelectron kinetic energy on the vibration of the residual photoion over an extremely broad range (ΔEk ≈ 100 eV). One might think that there would not be a strong interaction between electronic and nuclear degrees of freedom because the Franck-Condon approximation implies that vibration and electronic motion are decoupled. However, my results demonstrate that the photoelectron motion is correlated with the photoion vibration much more persistently than is usually assumed.

Absorption of a vacuum ultraviolet (VUV) photon by an isolated molecule provides sufficient energy for the molecule to access a variety of photoionization processes. For the moment, consider two possibilities – the creation of a stable molecular ion or creation of an unstable ion which decays via unimolecular decomposition. In either of these two cases, the outcome of the process can be monitored if the species are created in electronically excited states that decay via fluorescence. Some variations on these possibilities are sketched in Fig.1.1. A polyatomic molecule ABC is photoionized; process (a) refers to either singly or multiply charged, electronically excited stable parent ionic states which radiatively decay; process (b) refers to singly or multiply charged unstable ionic
states that dissociate into excited ionic fragments, where, \( p+q=n \); process (c) refers to the ion pair formation, where, \( n=0 \).

\[
\text{ABC} + h\nu_{\text{exc}} \rightarrow [\text{ABC}^{n+}]^* + \text{ne}^-
\]

(a) \hspace{1cm} (b) \hspace{1cm} (c)

\[
[\text{ABC}^{n+}] \quad [\text{AB}^p+]^* + [\text{C}^q+]^* \quad \text{AB}^+ + \text{C}^- \\
+ \quad h\nu_{\text{fl}}
\]

Figure 1.1 Possible decay channels following the photoionization of a polyatomic molecule ABC.

Experimentally, the molecular photoionization (scattering) parameters can be monitored with great precision [1]. One can tune the energy of the ejected photoelectron by adjusting the incident photon energy \( h\nu_{\text{exc}} \). Similarly, it is possible to interrogate the internal energy deposition of the ion by detecting the dispersed fluorescence from ions created in electronically excited states [2]. Measurements over a continuous and wide range of photon energies are needed to characterize the dynamical aspects of the process. Synchrotron radiation provides the tunable source of photons needed to study the continuous variation of
molecular photoionization cross sections with photon energy, and makes it possible to study the structure of the electronic continua of molecules at a highly differentiated level [3]. I will show that dispersed fluorescence experiments, along with theoretical developments, have led to remarkable progress in our understanding of the dynamics of molecular photoionization. In particular, the ability to study electron and nuclear motion correlations over a broad energy range provides a global view of the process, and generates useful insights into fundamental molecular scattering phenomena.

Normally, it is assumed that the Franck-Condon approximation applies to dipole transitions, including molecular photoionization. In this framework, one predicts that there will be no connection between the photoelectron kinetic energy and the photoion vibration. However, such a viewpoint neglects the highly anisotropic molecular potential experienced by the outgoing electron, and these molecular aspects have tremendous leverage over the coupling between electronic motion and nuclear motion [4-8]. We shall see that shape resonances in which photoelectron is temporarily trapped by a potential barrier play an important role in molecular photoionization, and therefore these shape resonances are the focal point of many experimental and theoretical studies of molecular photoionization.

1.1 Motivation

In fact, the connection between electronic and nuclear degrees of freedom is the central issue addressed in this thesis, and forms the primary motivation for studying photoionization dynamics [9-21]. Photoionization creates a collision complex that subsequently decays by ejection of an electron, and the outgoing
electron carries vital information about molecular physics: the electron scattering in the anisotropic molecular potential and the interplay between the electronic and nuclear degrees of freedom. This information can be accessed by highly resolved photoionization data. For example, by sampling alternative vibrational modes, these data probe the sensitivity of the ionization dynamics to changes in molecular geometry. Moreover, it is possible to do this in a mode specific manner for polyatomic vibrational motion.

In order to make significant progress in this research, it is necessary to forge strong connections between the experiment and theory. In particular, it is important to make direct comparisons, when possible, and for experiments to probe new aspects that challenge theoretical efforts to move in new directions. One of the first characteristics to evaluate in molecular photoionization dynamics is the overall photon energy dependence of the partial cross section and angular distribution parameters. Technical advances, especially the availability of synchrotron radiation [3], have enabled experiments to provide stringent tests for theories and to serve as stimulants for their further development by which we can gain additional quantitative and physical insights into the underlying dynamics of molecular photoionization. This dissertation strives to serve this role by providing new information on polyatomic shape resonant photoionization dynamics and dissociative photoionization dynamics.

Thirdly, there has been an intensive effort at correlating energy shifts of shape resonances in Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra with changes in a specific bond length in polyatomic molecules [22-24] (here, shape resonant ejection of core electrons). Such structure correlations are
motivated by the need to characterize the structure of adsorbates on surfaces. To provide a solid foundation for such efforts, it is essential for us to have a detailed understanding of molecular aspects affecting the photoionization dynamics. Earlier vibrationally resolved studies of the $7\sigma^{-1}$ photoionization of $\text{N}_2\text{O}$ [25], including two studies by our group [26,27], demonstrated that interpretations that assume that the shape resonance wavefunction is localized on a specific bond in the molecule is not universally valid. These results motivate current vibrationally resolved investigations of other polyatomic systems. In particular, it is necessary to look for and understand the ramifications of resonances in other vibrational modes, and one of the goals of this thesis project is to investigate the sensitivity of shape resonances to bending modes, which arise in polyatomics.

It has been found that resonant excitation of $\text{C}_2\text{H}_2$ leads to substantial excitation of bending mode in the photoelectron spectrum [28,29], but it is not clear if the resonance that is responsible is a shape resonance or an autoionization resonance. My studies on $\text{N}_2\text{O}$ and $\text{CO}_2$ are much more straightforward because there are well-defined shape resonances for these systems. It is still somewhat difficult to perform these types of studies, because the transitions that we are attempting to detect are weak. Fortunately, our recent experimental advances have made the required vibrationally resolved data much more accessible [12].

Finally, a qualitative microscopic understanding of molecular scattering dynamics requires probes that provide information on molecular aspects of photoionization process (i.e., vibration, rotation, alignment, dissociation) over a broad energy range. It is the purpose of this dissertation to provide new experimental results on vibrationally resolved shape resonant photoionization and
dissociative photoionization of polyatomic molecules. Polyatomic molecules are particularly attractive for investigations of shape resonances because there are alternative vibrational modes which are available for study [30]. Specifically, different internuclear configurations are probed by selectively sampling alternative vibrational levels of the ion; transitions to alternative vibrational levels of the ion preferentially weight different molecular geometries, leading to resonance positions and widths which vary with vibrational channels. Thus, the rich continuum electron trapping mechanisms can be mapped and qualitative aspects of the electron ejection are illuminated. Ultimately, it is hoped that studies of the response of the shape resonance to alternative vibrational modes can be utilized to obtain a more detailed spatial map of the continuum wavefunction [25,27,30]. Such information on vibrational dynamics helps to establish the trapping site of the resonant state on the molecular framework. As we will see, the vibrationally resolved studies of shape resonant excitation demonstrate that the bending degree of freedom is complementary to the existing studies that are either vibrationally unresolved, or those that probe only stretching degrees of freedom.

The studies of vibrational distributions of fragment ions is a more speculative experiment. However, there is very little known on the dissociation dynamics in this region of the spectrum, and it is hoped that the initial results that I have obtained can stimulate considerably more activity in this area. There is a tremendous potential for x-ray photochemistry to develop, as so many practical applications can emerge in the areas of x-ray lithography and micromachining. However, the ability to design such processes systematically requires an understanding of the dissociative pathways which are responsible for the ensuing
chemistry. Determination of the final state distributions of fragments from the dissociative photoionization opens a window on the electronic and nuclear motion of the collision complex responsible for the asymptotic fragment distributions.

1.2 Outline of This Dissertation

The remainder of the dissertation is outlined as follows. In Chapter 2, I present background information and a review of the present state of understanding the role of molecular vibration in shape resonant photoionization in the outer-valence region. The discussion focuses on the Franck-Condon approximation applied to molecular photoionization. The overall photon energy dependence in shape resonance cases is discussed in detail. A brief discussion is given for the breakdown of molecular orbital picture phenomena and electron correlation effects in molecular photoionization in inner-valence.

Chapter 3 gives a detailed account of the experimental technique. The experimental strategy to probe the correlation between electronic and nuclear motion is discussed and compared with the complementary method of photoelectron spectroscopy. Information about the main components of the apparatus are presented.

Chapter 4 presents the results. Section 4.1 focuses on shape resonances in polyatomic molecules. Vibrationally resolved data for the $7\sigma^{-1}$ photoionization of $N_2O$ and $3\sigma_u^{-1}$ photoionization of $CO_2$ are presented. Implications of these studies are discussed, and comparisons for these two isoelectronic systems are made regarding the shape resonance effects on bending vibration. Section 4.2 presents the results from vibrationally resolved fluorescence measurements of
ionic fragments $N_2^+(B^2\Sigma_u^+)$ following dissociative single and double photoionization of $N_2O$. Dissociation onsets of the dissociation process and the internal energy distributions for the fragments are discussed in detail.

Chapter 5 summarizes the accomplishments of the experimental efforts and future work are suggested.
Chapter 2

Background and Literature Review

2.1 Introduction

For photoionization of randomly-oriented gas-phase non-chiral molecules, the differential electronic partial channel cross section is given [31]

\[
\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[ 1 + \beta P_2(\cos \theta) \right]
\]

(2.1)

where

\[
P_2(\cos \theta) = \frac{3\cos^2 \theta - 1}{2}
\]

(2.2)

is the second-degree Legendre polynomial, \( \theta \) is the angle between the polarization vector of incident light and the direction of the ejected photoelectron. The cross-section, \( \sigma \), is the quantity that we measure. \( \beta \) is the angular anisotropy parameter, which reflects the nature of the orbital from which the electron is ejected, and depends on incident photon energy because of changes in the interaction of the continuum channels into which the photoelectron is ejected. For photon energies below about 10 KeV, the photoionization cross section equals the photoabsorption cross section since other processes which attenuate photons are negligible. Measurements of cross sections require studies over a continuous wide range of photon energies in order to make realistic comparisons with theory, and to investigate resonances. Such a source of photons is synchrotron radiation, and
will be discussed in the chapter 3. It should be mentioned that a study of $\beta$ as a function of photon energy is an ideal complement to data on the partial cross sections.

One-photon, single ionization is usually studied by assuming that the photon field can be treated classically [11]. The photoionization cross section is then obtained from the first-order transition rate between the initial state and the final excited state. The initial target state in most cases is the ground electronic state of the neutral molecule, and the final state has a photoelectron in the molecular electronic continuum. The initial state is generally represented by a Hartree-Fock or configuration interaction (CI) wave function [11]. The continuum orbitals of the final state are more difficult to obtain. These difficulties arise primarily from the nonspherical potentials of molecular ions and the necessity to include exchange effects in the potentials. The standard quantum chemistry procedures can not be used directly to solve the continuum problem. First, bound-state wave functions are square integrable $L^2$ and can thus be expanded in $L^2$ basis functions, e.g. Slater functions or Cartesian Gaussian functions. In contrast to this, the continuum functions can not be expanded in $L^2$ basis sets [32]. Secondly, for continuum states, Rayleigh-Ritz variational expressions for the energy can not be used [32]. However, the continuum electronic problem is amenable to the same physical approximations as is the bound-state problem. We can consider the independent-particle approximation, or Hartree-Fock approximation, as the simplest form of the many electron wave functions. This approximation can be improved by including electron correlation effects.
There are two main resonant processes in photoionization, and they can be classified as one- and two-electron resonances. A one-electron resonance is due to the average potential which the photoelectron feels. When this independent-particle or Hartree-Fock potential for the photoelectron supports resonant states which are above the ionization threshold in energy, they manifest themselves as *shape resonances* [4]. The name, shape resonance, comes from the fact that the resonance is produced by the shape of a single-particle potential [1, 33-35]. Two-electron resonances, *electronic autoionization resonances*, are due to electronically excited quasi-discrete states of one channel which lie above the ionization threshold for another channel. Because these autoionizing states lie above the threshold for ionization, they can decay into an adjacent continuum target state via two-electron processes. The electron ejected by autoionization carries away the energy difference between the initial ground- and final-state ion. The energy difference can be exactly that corresponding to direct photoionization. Thus, these two processes are indistinguishable in terms of kinetic energy of the ejected electrons. However, the branching ratios for the different final vibrational states, the cross sections, and the $\beta$ values are usually quite different, being dependent on entirely difference of the processes. Therefore, from the nature of these resonant processes, a Hartree-Fock level description of the photoionization is suitable for the one-electron resonances, but electron correlations must be included in the study of two-electron resonances.

The central point of molecular photoionization is that the escaping electron traverses the highly anisotropic potential of the molecular ion, and any subtle changes can strongly influence the scattering dynamics of the photoionization [4].
To understand the nature of scattering dynamics, one must consider both electronic and nuclear motion. The Franck-Condon approximation assumes that the nuclear vibration and electronic motion are decoupled, i.e., the electronic transition matrix element does not vary rapidly with internuclear geometry [4, 36]. For nonresonant photoionization, the final state vibrational distributions are in large part governed by the Franck-Condon principle, and hence the intensity of a given vibrational line is proportional to the square of the overlap matrix element between the initial neutral ground state vibrational wave function and the vibrational wave function of the final ionic state. However, when the photoionization cross section is enhanced by a shape resonance, the electronic transition matrix element can depend strongly on the internuclear coordinate [4,11,12], which means that the Franck-Condon approximation is no longer valid.

2.2 The Franck-Condon Approximation

The Franck-Condon approximation predicts that the electronic degrees of freedom of a molecule are uncoupled from nuclear modes of vibration during an electronic excitation [36,37]. The implications of the Franck-Condon approximation in molecular photoionization are made clear by constructing an expression for the transition matrix element $D$ of the electric dipole operator $\mu$, which governs the transition from the initial wave function $\Psi_{E0,v_0}(r,R)$ to the final state wave function $\Psi_{E+,v+}(r,R)$,
\[ D = \iint \Psi_{E^+, V^+} (r; R) \cdot \mu \cdot \Psi_{E_0, V_0} (r; R) \, d\tau_{\text{elec}} \, d\tau_{\text{nuc}} \quad (2.3) \]

The integrations are over all the electronic \((r)\) and nuclear \((R)\) coordinates. As with bound-state molecular systems, the Born-Oppenheimer approximation is generally valid, and hence the total molecular wave function can be factored into electronic and nuclear parts \(\Psi_E (r; R) \Psi_V (R)\) [36, 37]. So, we can rewrite equation 2.3 as follows.

\[ D = \iint \Psi_{E^+} (r; R) \, \Psi_{V^+} (R) \cdot \mu \cdot \Psi_{E_0} (r; R) \, \Psi_{V_0} (R) \, d\tau_{\text{elec}} \, d\tau_{\text{nuc}} \quad (2.4) \]

where,
- \(\Psi_{V_0} (R)\) is the initial state vibrational wavefunction of the natural molecule;
- \(\Psi_{V^+} (R)\) is the final state vibrational wavefunction for the photoion;
- \(\Psi_{E_0} (r; R)\) is the initial electronic bound state;
- \(\Psi_{E^+} (r; R)\) is the final electronic continuum state;
- \(\int d\tau_{\text{elec}}\) denotes integration over all coordinates of electrons;
- \(\int d\tau_{\text{nuc}}\) denotes integration over all nuclear coordinates.

The total electric dipole moment \(\mu\) is the sum of the nuclear dipole moment \(\mu_{\text{nuc.}}\) and the electronic dipole moment \(\mu_{\text{elec.}}\),

\[ \mu = \mu_{\text{nuc.}} + \mu_{\text{elec.}} \quad (2.5) \]

with

\[ \mu_{\text{nuc.}} = \sum_{\text{nuclei}} Z_i R_i \quad (2.6) \]
\[ \mu_{\text{elec.}} = -e \sum_{i} r_i \] 

(2.7)

Here, \( e \) is the electronic charge; \( Z_i \) is the atomic number of the \( i \)th nuclei with position vector \( \mathbf{R}_i \), \( r_i \) is the position vector for the \( i \)th electron. Since electronic wave functions \( \Psi_{E_0}(r; \mathbf{R}) \), \( \Psi_{E^+}(r; \mathbf{R}) \) are orthogonal,

\[
\begin{align*}
\iint \Psi_{E^+}(r; \mathbf{R}) \Psi_{V^+}(\mathbf{R}) \cdot \mu_{\text{nuc.}} \cdot \Psi_{E_0}(r; \mathbf{R}) \Psi_{V_0}(\mathbf{R}) \, dt_{\text{elec}} \, dt_{\text{nuc}} \\
= \int \Psi_{V^+}(\mathbf{R}) \cdot \mu_{\text{nuc.}} \cdot \Psi_{V_0}(\mathbf{R}) \, dt_{\text{nuc}} \cdot \int \Psi_{E^+}(r; \mathbf{R}) \Psi_{E_0}(r; \mathbf{R}) \, dt_{\text{elec}} \\
= 0
\end{align*}
\]

(2.8)

The Eq. 2.4 can be simplified as

\[
D = \iint \Psi_{E^+}(r; \mathbf{R}) \Psi_{V^+}(\mathbf{R}) \cdot \mu_{\text{elec.}} \cdot \Psi_{E_0}(r; \mathbf{R}) \Psi_{V_0}(\mathbf{R}) \, dt_{\text{elec}} \, dt_{\text{nuc}} 
\]

(2.9a)

\[
D = \int dt_{\text{nuc}} \Psi_{V^+}(\mathbf{R}) \left[ \int dt_{\text{elec}} \Psi_{E^+}(r; \mathbf{R}) \cdot \mu_{\text{elec.}} \cdot \Psi_{E_0}(r; \mathbf{R}) \right] \Psi_{V_0}(\mathbf{R}) 
\]

(2.9b)

\[
D = \int dt_{\text{nuc}} \Psi_{V^+}(\mathbf{R}) P_{\text{elec}} \Psi_{V_0}(\mathbf{R}) 
\]

(2.9c)

where the electronic transition dipole \( P_{\text{elec}} \) is defined as

\[
P_{\text{elec}} = \int dt_{\text{elec}} \Psi_{E^+}(r; \mathbf{R}) \cdot \mu_{\text{elec.}} \cdot \Psi_{E_0}(r; \mathbf{R}) 
\]

(2.10)

Note that \( P_{\text{elec}} \) depends on the incident photon energy (or, in other words, the photoelectron kinetic energy) through the final state continuum wave function \( \Psi_{E^+}(r; \mathbf{R}) \). It is at this point that we make the Franck-Condon approximation.
Namely, the Franck-Condon approximation assumes that $P_{\text{elec}}$ is a slowly varying function of the internuclear configuration. This allows us to rewrite Eq. 2.9c as follows.

$$D \approx P_{\text{elec}} \cdot \int d\tau_{\text{nuc}} \Psi_{V^+}(R) \Psi_{V_0}(R)$$

(2.9c)

Now we can examine the consequence of the Franck-Condon approximation on the photoionization process. The vibrationally resolved cross section $\sigma$ for photoionization is equal to the square of the matrix element $D$ of the total electric dipole operator $\mu$.

$$\sigma = |P_{\text{elec}}|^2 \cdot q_{if}$$

(2.11)

where

$$q_{if} = \left[ \int d\tau_{\text{nuc}} \Psi_{V^+}(R) \Psi_{V_0}(R) \right]^2$$

(2.12)

$q_{if}$ is the Franck-Condon factor.

Thus, the vibrationally resolved branching ratio, i.e., the ratio of cross sections for photoionization from the same initial bound state to alternative vibrational levels of the same final electronic state of the photoion, is then given by

$$\frac{\sigma_{if}}{\sigma_{if'}} = \frac{q_{if}}{q_{if'}}$$

(2.13)
which is independent of the excitation energy. It is important to note that the dependence of $\sigma$ on the excitation energy is contained entirely in the electronic dipole transition moment $P_{\text{elec}}$.

Equation 2.13 is the result of the Franck-Condon approximation applied to molecular photoionization. The Franck-Condon approximation provides an excellent picture of the ionization dynamics when there are no resonances in the ionization continuum. However, significant exceptions can arise if ionization proceeds via formation of a resonant complex. For example, in shape resonant photoionization, the ejected photoelectron is temporarily trapped inside the ionic core and has sufficient time to interact with its nuclear modes before escaping into the continuum. Hence, the trapping of the outgoing electron strongly enhances the overlap between the wave functions for the initial and final states, and the cross section curve exhibits a resonance enhancement. In fact, the Franck-Condon approximation frequently breaks down due to shape resonant processes [1-12]. Mathematically, the separation of the electronic and nuclear degrees of freedom in Eq. 2.9 is no longer valid, and as a result, vibrational branching ratios at resonance energies can deviate significantly from their non-resonant values. Therefore, Franck-Condon breakdown can serve as a tool to probe correlations between the electronic and nuclear degrees of freedom, and can help identify and characterize resonances in molecular photoionization. This approach has been widely used in the studies of shape resonances [2, 5-8, 12, 26, 27, 38-40]. Detailed discussions of how this strategy is employed in the current studies will be given in experimental method chapter.
2.3 Shape Resonances

Shape resonances play a prominent role in molecular photoionization dynamics [13-15,32] and have been observed in photoionization spectra for a large collection of molecules [4]. The effects of shape resonances can be examined experimentally by several means. One signature is an enhancement in the partial photoionization cross section. Shape resonances also result in changes in photoelectron angular distributions and vibrational branching ratios as a function of photon energy, both of which are manifestations of non-Franck-Condon behavior [40]. The predominantly one-electron nature of shape resonances lends itself to theoretical treatments within the independent-particle framework [17,20,32], which makes shape resonances relatively simple to study. As a result, there have been tremendous efforts, theoretical as well as experimental, focused on understanding the role of shape resonances in molecular photoionization since they were first discovered in photoabsorption studies of sulfur K- and L-shells in SF₆ more than two decades ago [41-43].

To understand the physics underlying shape resonances in molecular photoionization, it is useful to treat shape resonances in terms of a the single-channel, barrier-penetration model [4,44]. In order to illustrate some of the key points, it is useful to use an idealized one-dimensional model potential, and Fig. 2.1 shows such a representation of the effective local potential [1, 33-35] experienced by the photoelectron. This potential has three distinct features localized in distinct regions of space. There is an inner well that is formed due to strong attractive forces between the photoelectron and partially screened
molecular core at small distance. This well is highly anisotropic and extends over much of molecular charge distribution, i.e., it overlaps with the initial states of the photoionization process. A Coulomb-like tail exists at large distance (lying outside the molecule) where the photoelectron feels only the field of a unit

\[ E < E_r \]  
\[ E = E_r \]  
\[ E > E_r \]

Figure 2.1 Schematic of the effect of a potential barrier on the photoelectron as it leaves the molecular ion. The horizontal axis represents the distance of the photoelectron from the center of the ion (adapted from reference [44]).
positive charge (Coulomb potential \(-r^1\)). The inner well and Coulomb-like tail are separated by a repulsive potential barrier at intermediate distances. This barrier may arise ether due to a centrifugal potential \((\sim r^2)\), or an electrostatic repulsion arising from a high concentration of negative charge on the perimeter of the molecular ion [4] (e.g. SF$_6$). The attractive and repulsive forces compete with each other and are dominant in different regions of space. At small and large distances, attractive forces are dominant, but at intermediate distance, repulsive forces are stronger than attractive forces thus resulting in a net positive potential barrier that is localized on the periphery of the molecular charge distribution.

Insights into the dynamics of the photoelectron can be obtained by examining the effect of the potential barrier on the photoelectron wave function at different kinetic energies, as illustrated in Fig. 2.1 (dashed line). The electron can be trapped in the inner well for one or more values of kinetic energy. For the energies not equal to a resonance energy, the photoelectron wave function penetrates the inner part of the classically forbidden barrier, and merges into the Coulomb-like tail with much larger amplitude than in the inner well. This implies that inner well does not support the quasibound state at non-resonant energies; the wave function of the electron is not an eigenfunction of the inner well. At the resonance energy, however, the photoelectron wave function exhibits exponential decay in the barrier region and shows a monatomic decrease until it reemerges into the Coulomb-like tail with much smaller amplitude. The electron is thus trapped in the inner well but eventually tunnels through the potential barrier into the continuum. As a result, the resonant states supported by the inner well are quasibound. The name, "shape resonance," is derived from the fact that its origin
depends on the shape of the potential. The energy width of the resonance is related to the lifetime of the quasibound state.

To demonstrate the significant features of shape resonance in molecular photoionization, the remainder of this section turns to the specific examples of the well-known $N_2 \ 3\sigma_g \rightarrow k\sigma_u$ shape resonance [35, 45-50] and the $N_2O\ 7\sigma \rightarrow k\sigma$ shape resonance [30, 51]. The potential barrier responsible for the trapping of the photoelectron is sensitive to the internuclear configuration, which is the balance between the attractive and repulsive forces on the outgoing photoelectron. Slight changes in the molecular geometry can shift this balance, thereby altering the potential barrier. Such sensitivity of shape resonances to internuclear configuration was first predicted by the multiple scattering model calculations for $3\sigma_g \rightarrow k\sigma_u$ photoionization of $N_2$ [40]. The channel accesses the $\sigma_u$ shape resonance at ~ 14 eV above the threshold. At larger $R$, the inner well of the effective potential acting on the $l = 3$ component is more attractive and the shape resonance shifts to lower kinetic energy, being narrower and higher. As $R$ decreases, the shape resonance shifts to higher kinetic energies and the resonance becomes weaker and border. This is explained by theoretical calculations [40] which show that for lower values of $R$, the potential experienced by the photoelectron becomes more repulsive. Thus, the trapping of the shape resonant electron is weaker and needs less energy to overcome the barrier. This results in a shift of the resonance position to a higher kinetic energy, and a broadening over a wider energy range.

Effects of nuclear motion on individual final vibrational levels of the ion can be explained from the earlier theoretical analysis [40]. Since the levels of $v^+$
$v^+ = 1$ and $v^+ = 2$ sample the smaller $R$-values owing to their maximum overlap with the ground state vibrational wave function of the neutral molecule, the resonance position is shifted to higher kinetic energies than that for $v^+ = 0$. The impact of these effects on vibrational branching ratio as a function of incident photon energy is shown in Fig. 2.2.

Figure 2.2 Franck-Condon breakdown in $3\sigma_g^{-1}$ photoionization of N$_2$. Vibrational branching ratios vary drastically with the photon energy. Experimental (error bar) and theoretical (dashed line) results are from references [45] and [48], respectively.
Much of our understanding of the role of shape resonances in vibrationally resolved photoelectron spectra is based on the simple picture of their behavior in diatomics. The well-known sensitivity of shape resonances to bond length in the diatomic molecules [22] forms an important basis of our understanding of shape resonances for these systems. Shape resonant behavior in polyatomics is expected to be richer than in the simpler diatomic molecules due to the variations in chemical environments that might be sampled by an outgoing photoelectron. Moreover, there is the possibility of studying polyatomic shape resonances with considerably greater attention to detail, as the additional vibrational degrees of freedom that they offer provide additional degrees of freedom to study and probe. One interesting question that was studied previously is whether the shape resonant electron is trapped primarily in specific regions of the molecule, i.e., a specific bond of the molecule, or would be associated with the molecular framework as a whole [26,27]. Calculated photoionization cross sections for the 7σ level of N₂O at 16 internuclear geometries [30] show that the resonance moves to lower or higher energies with an increase or decrease respectively in either the N-N or N-O bond length. It is interesting to note that the position and the width of the resonance depends primarily on the overall length of the molecule and not on the individual N-N or N-O bond length. N₂O provides an interesting example of how shape resonance can influence alternative vibrational modes in polyatomics. The correlation of shape resonance position with "molecular size" lends to the idea that the enhanced amplitude of the photoelectron wave function extends over the entire molecular framework.
This contention is further illustrated in bending modes study presented in this dissertation. Bending degrees of freedom exist in polyatomics, and the bending vibration changes the "molecular size" in another fashion. In stead of changing the length of the molecule by stretching degrees of freedom, the bending vibration changes the width of the "box" where the ejected photoelectron is trapped. Therefore, this bending motion is expected to have much more profound effects on shape resonant photoionization dynamics.

The effects of shape resonances can be even more wide ranging: channels which are normally nonresonant at the Hartree-Fock level of approximation can "borrow" shape resonant character from other ionization channels via electron correlations (will be discussed in sec. 2.4) or via continuum channel coupling [52-55]. The interchannel coupling results in the sharing of oscillator strength between the ionization channels, and as a consequence, vibrational branching ratios also exhibit deviations from the Franck-Condon approximation.

2.4 The Breakdown of Molecular Orbital Picture in Inner-Valence Region

Part of my thesis work has been to understand the dissociative ionization fragmentation pathways that occur when electrons are ejected from gas-phase molecules. Particularly, some of these pathways involve the excitation of inner-valence electrons. The behavior of ionization processes following inner-valence shell ionization can be quite different from either core or outer-valence electrons, and in particular, it is frequently observed that Koopmans' theorem is violated.
Koopmans' theorem [56] is the identification of the ionization energy of a molecule with the energy of an electron in a molecular orbital, i.e., the ionization potential of the electron in the orbital $\Phi_i$ equals to the HF orbital energy $E_i$. His approximation describes the ionization process in terms of a single electron, so that the readjustment of the orbitals of the residual electrons which occurs after the removal of an electron has been ignored. Electron correlation is not considered in the self-consistent field (SCF) model of the independent electrons, and the results from Koopmans’ theorem are usually valid in outer-valence region [57].

The breakdown of Koopmans’ theorem in the inner-valence region is well established [58-65]. The origin of the phenomenon is the quasi-degeneracy of the inner-valence single-hole configuration (1h) with certain ionic configurations representing two holes in the outer-valence orbital and one electron in a virtual orbital (2h-1p). The interaction of these quasi-degenerate configurations via residual electron-electron interactions lead to a redistribution of the intensity associated with the inner-valence orbital. If the interaction is strong enough, the intensity of main lines may be distributed over numerous lines and it is no longer possible to discern between the main lines and satellite lines. This effect has been termed the breakdown of molecular orbital (MO) picture [66, 67]. The effects of electron correlation on photoionization processes are frequently obtained via photoelectron spectra [66-69].

Two important factors of relevance in the interpretation of the breakdown of MO phenomenon are the near-degeneracy and the magnitude of the coupling between the single-hole configuration and the 2h-1p configurations [66]. A near-
The degeneracy of the single-hole configuration with other ionic configurations is a prerequisite for MO picture breakdown. The coupling is expected to be large if the virtual orbital is localized in space as the occupied orbitals are. In the first-order perturbation theory, the position of a shape resonance in the electron scattering cross section is given by the virtual orbital energy [70]. In other words, the presence of a long-lived narrow resonance in space is a indication of the localized character of the corresponding unoccupied orbital, favoring the occurrence of the breakdown phenomenon. Moreover, the density of the ionic configurations is generally high in the higher energy region of the ionization spectrum, the matrix elements for the coupling of these configurations with the single-hole state must be large. Many satellite lines are expected to acquire their intensities from the main line.

The specific features of the breakdown phenomenon certainly depend on various properties of molecules under consideration, for example, size, symmetry, type of atoms involved, and most of all, their bonding properties [71-74]. In general, the higher density of 2h-1p configurations are observed for larger molecules of low symmetry. On the other hand, the nature of chemical bonding controls the coupling of 1h and 2h-1p configurations, and is, thus, a major factor influencing the form of the ionization spectrum.

Finally, while the breakdown of MO picture is common phenomenon in the inner-valence region, very little work has been carried out on the ionization cross sections in that energy region. Strong electron correlation effects and interchannel couplings complicate the problem. Considerable experimental and theoretical effects are required to clarify the role of the diverse effects.
contributing to these cross sections. Note that one-electron molecular orbital model works better for inner shell ionizations than for inner-valence ionizations. Because the inner shell hole is more localized in the atom, this small physical extent makes the mixing with the valence states negligibly weak [75]. Although some satellite lines appear in X-ray photoelectron spectra [76], the MO picture is valid in the inner shell energy region.
Chapter 3

Experimental Techniques

3.1 Experimental Strategy

In the previous chapter, it is suggested that measurements of partial cross section over a continuous and wide range of photon energies are needed to characterize the dynamical aspects of the molecular photoionization process. In particular, probing the breakdown of the Franck-Condon approximation is useful for characterizing resonant features that induce coupling between the electronic and nuclear degrees of freedom. This non-Franck-Condon behavior results in vibrational branching ratios changing with incident photon energy. It is the measurement of vibrational branching ratio as a function of incident energy that forms our experiment strategy for studying molecular photoionization dynamics.

Obviously, it is essential that experiments can selectively sample alternative vibrational levels of the photoion, as different vibrational levels probe alternative internuclear configurations. This requirement for vibrationally resolved data is a strong motivation for dispersed fluorescence measurements from the photoion. In this chapter, I give a detailed description of this method which enables us to obtain highly resolved vibrational (and rotational) data to characterize resonant and dissociation features in molecular photoionization.
To effectively carry out an experimental program on the partial cross section and vibrational branching ratio measurements, one requires: first, a photon source whose energies are continuous over a wide range in the ionization continua in order to probe and characterize the resonant features; second, such a photon source must supply a high photon flux to obtain reasonably well-resolved signals; third, the resolution should be high enough to access information at the vibrational (or rotational) level of detail. The photon source that accomplishes the above goals is synchrotron radiation [77, 78]. While synchrotron radiation sources are tunable, they do not simultaneously provide a narrow bandpass and a high flux of photons. In fact, the bandpass increases with the energy of the incident radiation [78, 79]. Therefore, one can not use conventional photoelectron spectroscopy to obtain high resolution data, because such a technique relies on detecting the ejected photoelectron as a function of the kinetic energy. A typical vibrationally resolved photoelectron spectrum consists of narrow peaks corresponding to alternative vibrational levels of final photoion states and these peaks are separated by energies \( \Delta E_{\text{vib}} \) \( (E_k = h\nu - \text{I.P.} - E_{\text{vib,rot}}) \), the \( E_{\text{vib,rot}} \) depends on the vibrational and rotational energy of the photoion; in photoelectron spectroscopy the rotational levels are rarely resolved. Most molecules have vibrational spacings \( \Delta E_{\text{vib}} \sim 10-1000 \text{ meV} \) and rotational spacings are smaller, \( \Delta E_{\text{rot}} \sim 0.1-1 \text{ meV} \) [80]. The bandpass of the incident radiation is \( \Delta E_{\text{exe}} \sim 100 \text{ meV} \) [78, 79]. As a result, the bandpass of the incident radiation reflected as uncertainty in the photoelectron kinetic energy is sufficient to wash out the vibrational structure in photoelectron spectrum. Mainly it is the excitation bandwidth that limits the resolution of photoelectron spectroscopy. It is
necessary to seek an alternative strategy that would decouple the excitation bandwidth from the detection channel, i.e., *the bandwidth of the optical detection system remains unchanged while tuning the incident photon energy*. Dispersed fluorescence measurement from electronically excited photoions serves this purpose perfectly.

To describe this strategy, the $2\sigma_u^{-1}$ photoionization of $N_2$ is used as an example. The excitation/decay sequence for this study is summarized in equation (3.1) and is illustrated in Fig. 3.1.

$$N_2[X^1\Sigma_g^+, v_0=0] + h\nu_{exc} \rightarrow N_2^+[B^2\Sigma_u^+, v^+] + e^-$$

$$\downarrow$$

$$N_2^+[X^2\Sigma_g^+, v'''] + h\nu_{v^+v''}$$

(3.1)

Here, $v_0$, $v^+$, $v'''$ are the vibrational quantum numbers for the neutral molecule, the excited state ion and the ground state ion, respectively. $N_2$ molecules in the ground state ($X^1\Sigma_g^+, v_0=0$) are photoionized to an excited electronic ionic state ($B^2\Sigma_u^+, v^+$), and within this electronically excited manifold photoions are distributed among different vibrational levels $v^+$. The excited photoions eventually decay to the ionic ground state ($X^2\Sigma_g^+, v''$) by emitting a fluorescence photon $h\nu_{v^+v''}$. The intensity $I_{v^+v''}$ of the fluorescence transition originating from a vibrational level $v^+$ is proportional to the number of ions in that vibrational level. The fluorescence cross section is proportional to the
partial photoionization cross section $\sigma_{v^+}$ for the vibrational level $v^+$. Thus, by monitoring the intensity of a fluorescence transition from a specific vibrational level $v^+$ of the ionic state as a function of the excitation energy, a constant-ionic-state (CIS) spectrum is generated. In practice, several CIS scans are generated simultaneously by using an optical multichannel analyzer (OMA) as
a detector. A ratio of any two such CIS spectra for alternative vibrational levels yields the corresponding vibrational branching ratio profile as a function of the incident photon energy. Note that the ratio of fluorescence intensities from alternative vibrational levels is not equal to the vibrational branching ratio [12]. This is because different upper vibrational levels are connected to the vibrational levels of lower neutral electronic state via Franck-Condon factors (FCF). The quantitative expression for the vibrational branching ratio can be written [12,81]

$$\frac{\sigma_{v_2^+}}{\sigma_{v_1^+}} = \frac{I_{v_2^+v_2^*}}{I_{v_1^+v_1^*}} \cdot \frac{q_{v_1^+v_1^*}}{q_{v_2^+v_2^*}} \left[ \frac{v_{v_1^+v_1^*}}{v_{v_2^+v_2^*}} \right]^3$$  \hspace{1cm} (3.2)

This equation shows that the vibrational branching ratio is equal to the ratio of intensities of fluorescence transitions originating from respective excited ionic state vibrational levels and FCFs. In other words, dispersed fluorescence measurement can be used to generate the desired vibrational branching ratio.

It should be emphasized that photoelectron spectroscopy does provide information on the energies for the photoionization processes; it also allows us to study the relative cross section for each individual process. However, there are differences between photoelectron spectroscopy and dispersed fluorescence technique, and it is important to appreciate their strengths and their limitations. The dispersed fluorescence measurement offers following advantages:

(a) The resolution of the technique depends only on the optical system (i.e., the dispersion and the slit width of a fluorescence monochromator), and is unaffected by the bandpass of the incident radiation. This is the key advantage over
photoelectron spectroscopy which enables us to obtain highly resolved photoionization data far from the ionization threshold.

(b) The collection efficiency of a fluorescence monochromator is typically one order of magnitude higher than that of electron spectrometers; plus, higher sample densities can be used in fluorescence measurements under the condition that secondary processes such as electron-impact ionizations are not occurring. Those advantages make studying weak ionization channels possible.

Although these advantages make a strong case for fluorescence measurement, there are limitations:

(a) Sample limitations: fluorescence measurements are limited to excited states of ions that decay radiatively. It precludes many excited ions that decay via fragmentation rather than fluorescence [82-85]. Therefore, the number of samples that can be studied by dispersed fluorescence is largely limited. The choices of samples are further limited when there are overlapping fluorescence transitions in the wavelength region of interest, although the same can be said for photoelectron spectrum peak congestion.

(b) The mechanism of formation of the excited ionic states can be ambiguous. Since the excitation bandwidth is decoupled from the fluorescence bandwidth, fluorescence measurements do not differentiate between the excited ions formed by photoionization of neutral molecules in the ground vibrational state and those from the excited vibrational states (i.e., the hot band excitation) [86,87]. The fluorescence transition has the same wavelength in both cases. In photoelectron spectroscopy, however, it is possible to differentiate between the two cases as
photoelectrons have different kinetic energies from different initial states of the target molecules. Moreover, it is possible that the excited ionic states of interest are populated partially by cascading from high-lying excited states of the ion. Fluorescence measurements are affected by such processes. In contrast, cascading has no effect on photoelectron measurements.

The above comparisons make it clear that the dispersed fluorescence and photoelectron spectroscopy provide complementary benefits. Since photoelectron spectroscopy is generally unable to provide the necessary resolution except for energies very near the thresholds, photoelectron spectroscopy is the useful technique at low electron kinetic energies. When vibrational resolved measurements on the photoion are required at higher photon energies, fluorescence spectroscopy is preferable. The complementary nature of these two techniques is clearly demonstrated in the N₂O study [25].

3.2 Experimental Apparatus

3.2.1 Synchrotron Radiation: CAMD-PGM

The principal arrangement of the experimental apparatus is presented schematically in Fig.3.2. Synchrotron radiation from the Center for Advanced Microstructures and devices (CAMD) facility [88] is used as excitation source in my experiments.

Synchrotron radiation arises from acceleration of relativistic charged particles. Many facilities dedicated to the use of synchrotron radiation are storage
rings in which electrons are circulated at energies in the neighborhood of 1 GeV to produce usable radiation up to about several keV. In addition, wiggler undulators [77] are being increasingly used to enhance the intensities and energies of the source. For experimental studies on photoelectron dynamics, it is often desirable to make measurements at energies considerably above the ionization threshold for the valence-shell (the order of 100 eV or more) binding energy. Moreover, one wishes to study effects near and above the core-shell binding energy; in the case of elements in the second row of the periodic table (carbon, nitrogen, oxygen, and fluorine), this implies a need for photons up to nearly 1 keV. Special studies on deeper core-shells of heavier elements may require...
even higher energy photons. Most of the experimental needs of photoelectron dynamics will be satisfied with a range of energies from 10 to 1000 eV. It is also necessary to disperse the incident radiation to obtain monochromatic beam. Monochromators are designed for efficiency, resolution and a particular energy range. For energies below the 1 keV, some kind of movable gratings are normally required.

The synchrotron radiation used in this work is produced from the electron storage ring at CAMD [88] at Louisiana State University (LSU). The machine operates at 1.3 GeV with beam currents of ~ 120 mA. The spectral output is dispersed by a 6-m soft x-ray plane grating monochromator (PGM) constructed by McPherson Instrument Co., see ref.[89]. The monochromator consists of a pair of crossed cylindrical mirrors (collimating and vertical) to focus the radiation onto a 3-cm-wide entrance slit. Passing through the entrance slit and four-jaw aperture, the light hits the movable pre-mirror, which translates and rotates, and is reflected to one of two interchangeable gratings. It is then focused onto the exit slit by a spherical mirror. Two gratings, interchangeable under vacuum, disperse the synchrotron radiation ranging from ~ 20 to 700 eV [90], and are suitable for studies of broad spectral features such as shape resonances and Cooper minima up to core-shell binding energies. The low energy grating has 360 grooves/mm and the high energy grating has 1220 grooves/mm. A 360 grooves/mm grating was used in this program. Through the focusing mirror, exit slit, a refocusing mirror, the light is focused to form a 1 mm square spot on the sample in the experimental chamber. The wavelength of incident radiation is scanned by using a drive screw that varies the rotation of grating. The drive
screw is driven by a stepper motor which is equipped with encoders to allow their absolute positions to be read by a computer. Beyond the refocusing mirror, there is a pneumatic window gate valve at the end of the beam line. Our experimental apparatus is coupled to the glass window gate valve port. The valve is interlocked by an ion gauge to protect the ultra high vacuum of the beamline.

The performance of the PGM beamline can be evaluated in terms of the intensity, resolution and higher order contamination. The incident photon flux is monitored by a tungsten mesh before the experimental chamber or by a windowless far UV photodiode (National Institute of Standards and Technology) mounted on the end of the experimental chamber. In the photodiode case, the diode consists of a mirror-like surface Al/Al₂O₃ photocathode suspended within a cylindrical anode with a Teflon body separating the two. The anode is maintained at a positive potential of ~ 60 eV. Incident VUV photons cause the emission of the low energy electrons that are collected by the anode. A calibrated picoammeter is connected to the photocathode to measure the rate of emission. The picoammeter current can be used to estimate the incident photon flux as follows, provided that the quantum efficiencies of photodiode are known. For example, in my experiments, a typical picoammeter current is ~ 5 nA, the quantum efficiency η of the photodiode is ~ 10 % at the energy range considered,

\[
5 \text{ nA} \sim 5 \times 10^{-9} \text{ A} = 5 \times 10^{-9} \text{ c/sec} = 5 \times 10^{-9} \times (1/1.6 \times 10^{-19}) \text{ e}/\text{sec} \\
\approx 10^{11} \text{ electrons/sec}
\]
Since the quantum efficiency $\eta$ of the photodiode is approximately 10%, that means 10 photons produces 1 electron, $10^{11}$ electrons/sec $\times$ 1/ (1 electrons/10 photons) = $10^{12}$ photons/sec.

The quantum efficiency of the photoemissive surface is defined as $\eta = \text{electrons emitted/photons absorbed}$. However, it should be noted that the quantum efficiency of photodiode may be altered by small amounts of surface contamination. Also, it should be ensured that the photodiode is protected from "unwanted" charged particles while operating, such as those from the ion gauge used to monitor the chamber pressure. Finally, the arrangement has an inherent drawback in that the incident photons have to pass through the interaction region before impinging on the photodiode. As a result, the photodiode output is not an exact measure of the incident photon flux since sample molecules absorb some of the incident photons. However, it should be noted that branching ratios are not affected by the normalization (see, chapter 2, Eq. 2.13). An alternative approach is to use a tungsten mesh to monitor the photon flux before it enters the experimental chamber. The tungsten mesh has a transmission coefficient $\sim 90\%$ and serves as an excellent monitor of the incident radiation [91].

The resolution of the PGM varies approximately linearly with the energy of incident photons [78,79], and is affected primarily by the exit slit width of the monochromator at the moderate resolutions. Normally, the entrance and exit slit widths are kept equal, but it is possible to obtain high flux without sacrificing the resolution substantially by opening up the entrance slit. The excitation bandwidth can be estimated by measuring the dispersed fluorescence of $N_2^+(B\rightarrow X)$ transition near the ionization threshold of $N_2^+(B)$ state ($\sim 18$ eV); and by
measuring the width of Al L-edge (~ 72 eV). 450μm, 600μm slit widths were used in the experiments, and the excitation bandwidths were estimated ~ 0.5 eV [5].

Finally, another important factor that needs to be considered is higher-order contamination. The output flux from each grating contains a significant contribution from higher-order diffracted radiation [77-79, 91]. When the monochromator is set to an energy E, the radiation coming out of the exit slit can also have energies 2E, 3E, and so on. The extent of the higher order radiation depends primarily on the grating geometry and mirror angles, especially the pre-mirror angle. High orders contribute to photoionization depending on their strength and the photoionization cross section of the sample at those energies [77, 78]. The preliminary results [91] from the CAMD-PGM for the low energy grating (360 groove/mm), fixed angles of the pre-mirror at 77.1° and 85°, and at fixed focus mode show one striking feature that there is low intensity of the second- and higher-order light at photon energy above 20 eV. This is largely due to the laminar profile of the grating [92]. In addition, the peak of the intensity curve shifts to higher photon energy as the angle of incidence is increased. This feature allows us to select an angle of incidence by maximizing the throughput of the monochromator for any photon energy ranges. In the fixed focus mode, the pre-mirror is scanned in tandem with the grating to keep the monochromator in focus, i.e., operating at smallest possible bandwidth. Note that the decrease in overall intensity and the increase in intensity of higher order light. As a conclusion, high intensity, high resolution, and minimum higher-order contamination can not be achieved simultaneously. One must select what is important for the experiments.
The higher-order contributions can be characterized by using photoelectron methods. Photoelectrons corresponding to different orders have different kinetic energies. At each photon energy, all the energetically accessible photoelectrons form peaks from the various orders of radiation. By checking the intensity of each peak in the photoelectron spectrum, we are able to tell the high-order contributions in the photon beam [91].

To reduce higher-order contamination, the simplest way is to use filters. Several elements have absorption edges which lie between 10 and 100 eV. Sn and Al filters are useful in the energy range $16 \leq h\nu_{exc} \leq 70$ eV. The filters have sharp cutoffs at $\sim 23.5$ eV and $\sim 70$ eV [93, 94, 95], for Sn and Al, respectively, when the incident photon energy is tuned below 23.5 eV or above 35 eV. They can, therefore, be used as transmission filters to eliminate the higher order contents.

### 3.2.2 Vacuum Considerations

Synchrotron radiation-based experiments have stringent vacuum requirements. Generally, storage rings and beamlines operate under ultrahigh vacuum (UHV) with pressure in the range $10^{-10}$ to $10^{-11}$ Torr. The sample in the experimental chamber is maintained at pressures approximately $10^{-3}$ to $10^{-4}$ Torr. Therefore, the experimental chamber must be isolated from the UHV beamline. This is achieved by the two-stage differential pumping in our experiment: differential pumping keeps the pressure in the first chamber before the beamline monochromator in the range of $10^{-10}$ Torr so that windowless experiment with gas
samples is possible without contaminations of the monochromator or storage ring. This technique is based on creating a huge conduction barrier to the motion of gas molecules from the experimental chamber to the beamline. An intermediate chamber is used between the experimental chamber and the beamline. Two glass capillary tubes of 2 mm inner diameter link the two differential pumping stages with ~1/8 inch gap between these two tubes and provide the requisite conduction barrier. At the same time, it serves the purpose of channeling the synchrotron radiation into the interaction region (discussed in sec. 3.2.4). The space between two capillary tubes is pumped by a 50 liters/s turbopump (Balzers, TPU 060). The intermediate chamber and the experimental chamber are pumped by a 500 liters/s turbopump (Balzers, TPU520) and a 2500 liters/s cryopump (Cryogenics, Cryo-Torr 10), respectively. In the experiments, a thermocouple gauge is used in the 1 torr to $10^{-3}$ Torr range; an ion gauge is employed to monitor the chamber pressure in $10^{-3}$ to $10^{-10}$ Torr range.

The pressure in the experimental chamber is typically maintained at ~$10^{-3}$ Torr during data taking. The stagnation pressure behind the nozzle is around 10 to 100 psi. Because of the small internal diameter of the capillary tubes, only a small amount of the sample gas is able to reach the region between the two tubes. As a result, most molecules in the differential pumping region are pumped away and very few that reach the intermediate chamber are then pumped away by the big turbopump. Using this setup, the pressure in the intermediate chamber can reach ~$10^{-10}$ Torr. The estimated value is $10^{-11}$ Torr (see ref. [96]). To reach such a ultrahigh vacuum, UHV techniques are essential in handling the surfaces of the vacuum chamber, as discussed in ref. [96].
In general, when a chamber is first pumped out, the bulk of the residual gas is water vapor. At low pressures, molecules desorbed from the walls make up the residual gas [97]. To achieve pressures much below $10^{-7}$ Torr, baking is required in order to remove water from the walls of a vacuum system. The intermediate chamber is baked at temperature $\sim 95^\circ$C for at least 12 hours. This improves the ultimate pressure by more than one order of magnitude. After a rigorous preliminary baking to remove deeply absorbed molecules, the system can be baked gently ($\sim 4$ hours) in case of a short time exposures to the air. Dry N$_2$ gas is ideal for venting and purging the chamber. The chamber is wrapped with heating tape and then covered with aluminum foil to ensure an uniform bake temperature over all the surfaces.

Finally, note that metallic foil windows can be used to isolate the experimental chamber from UHV beamlines. In our N$_2$ K-edge experiment, the thin metallic foil (Al:1%Si, 1500+/−100A thickness, Luxel Co.) supported on stainless steel mesh was installed within a gate value (VAT series 01) so that it could be moved in and out of the beamline with relative ease. The foil material has fairly high overall transmission (60%) in the energy range of interest ($400$ eV) [94], yet is sturdy enough to withstand pressure differentials. While the window setup opens up new energy ranges, there are several drawbacks. First, most foils do not transmit over an entire spectral range of interest so these foils are only useful for experiments over a relatively small range of incident radiation. One can find a set of foils to cover a large energy range, but it is cumbersome to interchange foils. Second, one just cannot connect the experimental chamber at atmospheric pressure to the beamline and close the gate valve to separate two.
The pressure difference will blow away the thin foil. To overcome this problem, the gate valve with the foil should be kept open while the experimental chamber is being pumped down. When the pressure decreases to about $10^{-3}$ Torr, the foil is put in by closing the gate valve. The beamline than can be open to the experimental chamber. Caution must be taken to prevent the foil from the radiation damage. When changing the incident energy by moving the grating (remote controlled), the photon shutter should be closed to avoid the zero order light damage. Third, reactive gases will induce pinholes in thin foils, which was observed in the C$_6$F$_6$ study. The choices of sample are somewhat limited in window setup experiments.

### 3.2.3 Sample handling: Supersonic free Jet

Two gas samples — N$_2$O, CO$_2$, are used in the experiments that I described in chapter 4. Samples are introduced through a supersonic free jet mounted on an XYZ manipulator. There are several advantages for using a supersonic jet instead of a gas cell: first, it replaces the conventional gas cell which absorbs substantial amount of incident radiation as well as fluorescence intensity being detected. Second, it provides a such high density of molecules in a extremely small volume that the interaction of molecules and incident radiation is effective. It is crucial to adjust the position of the gas jet so that the small volume is directly in the path of the incident beamline. We make this adjustment with an XYZ manipulator (Thermionics, EM-200 series). Third, it allows high resolution study of free molecules unperturbed even by gas phase collisions [98-102]. However, the most important advantage of using supersonic jet is its
ability to dramatically simplify molecule spectra by cooling a sample gas far below the normal temperature of condensation. This results in a highly resolved picture of complex molecular energy states. It is the rotational cooling that makes my hot band excitation work possible.

In principle, if the number of initial energy states is limited, the number of possible transitions is reduced and the spectrum can be simplified. The most practical way to limit the number of initial energy states is to lower the temperature of the gas molecules, because at low temperatures only the states of lowest energy are populated. Hence, the strategy for reducing spectral complexity is to measure the spectrum of the isolated molecules at low temperatures. At low temperatures achieved with traditional refrigeration methods, however, molecules tend to condense into the liquid or the solid state. Therefore, the problem is to make a gas cold enough to limit the number of initial energy states without allowing the gas to condense.

The laws of thermodynamics state that under appropriate conditions the expanding gas in a free jet must cool. On a microscopic scale, the cooling of a gas implies that the energy of the gas molecules associated with the random motion is reduced. The temperature in a free jet is measured by the width of the velocity distribution. Collisions among the molecules in the jet narrow the range of molecular speeds along the direction downstream from the nozzle, and so the molecules begin to move at nearly the same velocity. It is the narrowing of the velocity distribution that allows the gas to be cooled to within a few hundredths of a degree of absolute zero under ideal conditions.
As the expansion proceeds, the binary collision rate drops rapidly and a point called *Mach disk* is soon reached [102] as there too few collisions to affect an appreciable change in the velocity distribution. The cold molecules desired are located within the isentropic core, surrounded by barrel shock and the Mach disk. Therefore, it is very useful to estimate the *Mach distance* so that this small core can be positioned in the interaction center. For free jets with circular apertures, the Mach distance $X_m$ can be calculated using Eq. 3.3,

$$X_m = 0.67 D \left(\frac{P_0}{P_t}\right)^{1/2}$$  \hspace{1cm} (3.3)

where $D$ is the nozzle diameter, $P_0$ is the pre-expansion pressure of gas jet (called stagnation pressure), and $P_t$ is the chamber pressure [102]. The region of our interest within the isentropic expansion core typically starts five to ten nozzle distances downstream from the nozzle and extends to the Mach disk. If the nozzle size is 100 $\mu$m, the distance typically would be $\sim$ 1 mm from the interaction center.

The terminal temperature $T_T$ of a monatomic gas sample can be calculated using Eq.3.4,

$$\frac{T_T}{T_0} = \left[ 1 + 5896 \left(\frac{P_0 D}{P_t}\right)^{0.8} \right]^{-1}$$  \hspace{1cm} (3.4)

where $T_0$ is the stagnation temperature of the nozzle [102]. The equation 3.3 shows that as the nozzle diameter is increased, i.e., the expansion field becomes bigger, molecules must travel further to reach the Mach disk. Since a binary
collision is proportional to the pressure, the quantity $P_q D$ is proportional to the
total number of binary collisions a molecule makes before it achieves a given
Mach number. Equation 3.4 states that the terminal temperature is a function of
$P_0 D$, which implies that it is the total number of binary collision that makes the
cooling possible. Therefore, $P_0 D$ must be made as large as possible. On the
other hand, in order to minimize the extent of condensation, the ratio $D/P_0$ must
also be made as large as possible [103]. Overall, the net effect of these
requirements is to increase the mass flow through the nozzle. Also, gas mixing is
an effective way to cool gas molecules of spectroscopic interest to much lower
temperature. A small amount of sample is mixed with a large quantity of
monatomic carrier gases such as He, Ar, etc [103]. As long as the density of the
mixture is high enough, the molecules collide with the cold atoms, and the
energies associated with rotational and translational motions are transferred to the
translationally cold bath of the monatomic gas. The rotational and translational
coolings are more complete than vibrational cooling [99].

Finally, unlike cooling, which requires two colliding particles,
condensation is slow process because its initiation requires simultaneous collisions
among three or more particles. Three-body collisions require much higher
densities in the gas sample than two-body collisions do, and the cooling is
complete before a significant number of three-body collisions can take place. In
effect, the molecular gas is rapidly cooled below its ordinary condensation
temperature, and then allowed to expand.
3.2.4 Optics

Figure 3.2 illustrates the optical layout of experimental apparatus. Synchrotron radiation is channeled into the interaction region by two capillary tubes. The end of the capillary tube in the intermediate chamber is adjusted so that is positioned at the focal point of the refusing mirror. Since the radiation beam is almost horizontal (its divergence is ~ few milliradians, cross section is ~ 1 mm²), once the incident beam is captured by the capillary tube, it is channeled without much absorption and comes out at the other end having the same divergence. In the differential pumping region, two capillary tubes must be well aligned so that no light is lost during the transfer. In the experimental chamber, the other end of the capillary tube is positioned ~ 1 cm away from the interaction center so that the incident light intersects the gas beam at the focal point of collimating lens $L_1$. To locate this point, we have a pin mounted on a linear feedthrough. The tip of the pin is placed at the focus of the collimating lens ($L_1$) by driving the feedthrough in, then the incident beam and gas jet are adjusted with respect to it. The alignment is carried out with zero-order visible incident radiation. It helps to locate the beam spot so that the capillary tube can be steered in the right direction.

The fluorescence radiation from the interaction region is collected and collimated by a 100 mm focal length, 25 mm diameter plano-convex lens $L_1$, as the focal point of the lens is positioned at the interaction region. A 25 mm diameter, 100 mm focal length concave mirror is placed on the opposite side of the interaction region at a distance equal to its radius of curvature 200 mm. In
this configuration, any fluorescence radiation that hits the mirror will be reflected to retrace its path and then be collected by lens \( L_1 \). The collection efficiency is increased by about a factor of two. The collimated fluorescence exits the chamber through a window. Then, the collimated light is reflected onto the horizontal plane by a square plane mirror \( M \) (50 mm x 50 mm) and focused by second plano-convex lens \( L_2 \) (25 mm diameter, 125 mm focal length) onto the entrance slit of the fluorescence monochromator (Instrument SA, HR640). A mirror is placed inside the monochromator to reflect the dispersed fluorescence out perpendicularly to the exit slit.

There are three gratings available in our laboratory for the ISA HR 640 monochromator (1200 grooves/mm, 2400 grooves/mm, and 3600 groves/mm). For my studies, the gratings are used in first order as this gives high efficiency over a wide spectral range. The choice of the grating is governed by the spectral range of interest, the fluorescence intensity, and the resolution desired. A grating with a low reciprocal linear dispersion \( D^{-1} \) has low transmission efficiency [104]. One may not have many choices but to use a grating with high \( D^{-1} \) when the signal is weak. A related factor is the slit width. The choice of a slit width is basically a trade-off between the intensity and the resolution.

For efficient collection of light by a monochromator, the input f-number (of \( L_2 \)) must match the f-number of the monochromator [97,104]. This requirement determines the optimum focal length of lens \( L_2 \). Since the f-number of our monochromator is 5.2, and the lens diameter is 25 mm, the focal length of \( L_2 \) is constrained in the range of 130 mm (5.2 x 25mm). Moreover, the quality of the image formed on the entrance slit \( S_1 \) is also very critical. It should be as
small as possible so that small bandpass can be obtained by small slit widths without losing much intensity. It is critical to steer the light to the middle of the slit, and this is accomplished by mounting the lens $L_2$ on an XY linear drive inside the optical box so that it can be adjusted in parallel and perpendicular motion to the plane of the entrance slit $S_1$. The "pitch" of the fluorescence path is changed by adjusting the orientation of the mirror $M$ (see, fig. 3.2).

Finally, the efficiency of collecting the fluorescence photons from the interaction region depends primarily on distance of the focal point of lens $L_1$ and interaction center. Only those photons within the cone of $L_1$ at the interaction region are collected. Therefore, the focal length of $L_1$ is on the short side, 100 mm chosen as a good compromise. The overall collection efficiency of this optical system is estimated to be $\sim 0.38\%$ [96]. To minimize any possible losses, all the optical elements are chosen to obtain high transmittance for lenses and high reflectance for mirrors over a wide spectral range from $\sim 2000\text{A}$ to $\sim 7000\text{A}$. The above considerations ensure that the maximum amount of fluorescence is collected, transmitted, and finally detected. In the experiments, a He:Ne laser is used for the alignment of the optical systems: a laser beam is shone onto the pin placed at the interaction region; mirror $M$ and lens $L_2$ are carefully adjusted until a focused bright image is visible at the center of exit slit $S_2$.

3.2.5 Detectors

Because the signal levels are quite low in my experiments, it is important to detect the fluorescence radiation efficiently. This can be accomplished via
parallel detection, where an entire spectral region of interest is acquired simultaneously. Since spectral acquisition is a parallel process, scanning nonlinearities in traditional detection methods have been minimized. To achieve such a parallel detection, charged-coupled device (CCD) is used. CCDs consist of an array of diodes (called pixels, or channels), each acting as a light-to-charge transducer, a storage device and gathers a signal simultaneously to perform the unique task of manipulating information. They are suitable for low to ultra-low level light detections requiring very long integration times.

CCD is a large-scale integrated circuit fabricated on a silicon crystal [105]. The mechanism of CCD operation is illustrated in Fig. 3.3. A linear CCD

![Figure 3.3 Mechanism of CCD operation in storage and transfer modes. (a) CCD storage mode. (b) CCD transfer mode.](image-url)
device comprises an array of closely spaced metal-insulator-semiconductor (MIS) capacitors. Each MIS pixel consists of a conductive electrode and a thin oxide layer insulator on top of a semiconductor p-type silicon. When a positive voltage is applied to the electrode, a thermal charge depletion region called potential “well” is formed underneath the silicon. These potential wells serve as temporary individual storage elements for the photon-generated electrons (signal) as well as for the thermally generated electrons (dark current). The amount of charge accumulated is a linear function of the incident illumination intensity and the integration time. At the beginning of a measurement circule, the capacitive diode pixel is fully charged by a coupled tiny capacitor. The charge is stored on the reverse-biased p-n junction as well as between the p-type strips. On the illumination of the diode, charge leaks off the capacitor because of the appearance of signals and dark current. After the signals are obtained, each element of the array is scanned, and the capacitor is recharged. Readout is accomplished by using two TTL level signals, a start pulse, and a clock. Each photodiode is connected to the output line of a field effect transistor (FET) switch, which is controlled by a single bit that is shifted through the shift register. When the FET switch is addressed, the diode is charged up to its full reverse-bias potential. The integration time, which is same for all diodes, is the total time each diode integrates light before it is read out again.

There are several readout methods for a CCD, including real-time readout, the variable integration technique, diode binning, and “skipping” diodes [106]. Diode binning is the readout method used in my experiments. In diode binning, the adjacent diodes are electronically summed after digitization into
predefined groups. This is accomplished through the software. On the other hand, there is hardware binning, in which charge from separate pixels is added together on the horizontal shift register or in the preamplifier (or in both) before digitization. Since the noise associated with each readout is fixed, the hardware binning can result in a significant increase in S/N ratio. Moreover, since the digitization time for each charge is a fraction of the total readout time, there is a significant decrease in readout time by the hardware binning. The "pixel" created by binning several pixels together is called "superpixels". Ideally, the S/N ratio will improve linearly with the superpixel size. In practice, the noise increases slightly with the size of the superpixel. Therefore, it is better to use relatively small superpixels and add them together after digitization, i.e., using hardware binning first, then software binning. The other strategy for obtaining the largest signal is to increase the time between the readouts until the signal is just under the saturation (integrate the signal on-chip) [106]. On-chip integration improves the S/N ratio proportionally to the exposure time.

The attractive features of CCD devices are wide dynamic range and very low noise [106]. The dark current is a temperature-dependent noise source. It can be reduced to an insignificant level by cooling the array. Fluctuations in the detector temperature cause proportional fluctuations in the dark currents. Therefore, effective elimination of these fluctuations requires thermostating to within 0.001°C [105,106].

In my experiments, the intensity of dispersed fluorescence is measured by liquid-nitrogen cooled charge coupled devices (LN/CCD-1024-EUV, Princeton Instruments) mounted laterally to the monochromator. LN/CCD-1024-EUV has

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1024 pixels per array. The CCD is cooled to -100°C during the data taking. The
data acquisition is controlled by a PC/AT-type computer interfaced to a controller
(Princeton Instruments, model ST-130/135). Software package CSMA collects,
databases, process, and transfers the data from the detector to the computer.
Hardware binning by 5 was used in the experiments, many accumulation sweeps
(total on-chip integration time is about 30 minutes), and long exposure time (120
seconds) were employed to significantly improve the S/N ratio.
Chapter 4

Results and Discussion

4.1 Influence of Shape Resonances on Vibrational Behavior in Polyatomic Molecules

4.1.1 7σ⁻¹ Photoionization of N₂O

4.1.1.1 Introduction

There are several reasons why nitrous oxide (N₂O) was selected as the target system for the current study. First, it is a simple polyatomic molecule that is known to exhibit shape resonant behavior in the 7σ⁻¹ photoionization channel [25,26,27,30,51,107]. Previous investigations of N₂O photoionization by our group uncovered a breakdown of Franck-Condon approximation in the energy range 17-55 eV [26,27]. Vibrationally resolved data demonstrated how shape resonances are influenced by changes in molecular geometry. The cross section curves for alternative vibrational modes behave differently, i.e., symmetrical stretching exerts a greater influence on resonance behavior than the asymmetric stretching vibration. However, these data were taken on two different beamlines. "Stitching" the data from different beamlines together is prone to errors, so an
additional reason that $\text{N}_2\text{O}$ was chosen as a test case was to refine the earlier work.

Moreover, the current study addresses new issues that have never been addressed for polyatomic photoionization. First, the energy range of the current study far exceeds any previous vibrationally resolved photoionization study. The current study extends the energy range to $E_k = 220$ eV. A second new aspect of this work is that I have investigated the response of shape resonance behavior to the bending degree of freedom. In particular, I have studied how the bending vibrational motion of the ion is coupled to the photoelectron in the energy range $3 \leq E_k \leq 80$ eV. Collectively, these aspects of the $\text{N}_2\text{O}$ investigation allows us to obtain a survey into the qualitative trends of shape resonant photoionization dynamics for polyatomic molecules.

Nitrous oxide is a unsymmetric linear molecule (N-N-O, point group $\text{C}_{\infty v}$), resulting in three normal modes (degenerate bending mode), and hence, three vibrational quantum numbers. The ground electronic configuration of $\text{N}_2\text{O}$ is: $\text{KKK} \, (4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^4, \text{X}^1\Sigma^+$. Removal of an electron from the $2\pi, 7\sigma, 1\pi$, and $6\sigma$ orbitals produce the following electronic states of $\text{N}_2\text{O}^+$: $\text{X}^2\Pi = 12.89$ eV, $\text{A}^2\Sigma^+ = 16.38$ eV, $\text{B}^2\Pi = 17.65$ eV, and $\text{C}^2\Sigma^+ = 20.11$ eV, respectively [108-111].

The resonant behavior of individual vibrational levels of the $\text{N}_2\text{O}^+ \, 7\sigma^{-1}$ state are probed by using synchrotron radiation excitation and dispersed fluorescence detection to determine vibrational branching ratios as a function of incident photon energy. The excitation/detection sequence for this system is given by Eq. 4.1,
\[ \text{N}_2\text{O} [\text{X}^1\Sigma^+, v_0=(0,0,0)] + h\nu \rightarrow \text{N}_2\text{O}^+ [\text{A}^2\Sigma^+, v^+ = (n_1^+, n_2^+, n_3^+)] + e^- \]
\[ \downarrow \]
\[ \rightarrow \text{N}_2\text{O}^+ [\text{X}^2\Pi, v'' = (n_1'', n_2'', n_3'')] + h\nu_{v^+v''} \]

\[(4.1)\]

The vibrational levels are denoted by \( v^+ \) and \( v'' \) for the upper electronic state \( (\text{A}^2\Sigma^+) \) and the lower electronic state \( (\text{X}^2\Pi) \) of \( \text{N}_2\text{O}^+ \), respectively; and \( n_1, n_2, n_3 \) represent the number of quanta for the symmetric stretch, bending, and asymmetric stretch modes, respectively. Figure 4.1 shows a sketch representing the vibrational motions of the ion in \( v^+ = (1,0,0), v^+ = (0,0,1) \), and \( v^+ = (0,1,0) \).

Figure 4.1 A sketch illustrates how the end-to-end length of \( \text{N}_2\text{O} \) is affected by the symmetric and asymmetric stretching modes of vibrations. Bending vibration changes the width of the "box", which is trapping the ejected photoelectron.
states. The \( v^+ = (0,1,0) \) level of the ion is created primarily by photoionization of the neutral molecule with one quantum of vibrational excitation in the \( v_2 \) mode, not from \( v_0 = (0,0,0) \) \([86,87]\). The \( v^+ = (0,1,0) \) level of the ion is (relatively) heavily populated, which is surprising as photoionization studies have shown that the photoelectron intensity for this level relative to the \( (0,0,0) \) level is only 2.1\% \([110]\). Symmetry selection rules forbid the excitation of a single quantum of bending vibration \([108]\), although this mode maybe induced through vibronic coupling; in other words, in the absence of vibronic coupling, transition of \( v_0 = (0,0,0) \rightarrow v^+ = (0,1,0) \) can not happen upon photoionization. The fluorescence intensity originating from level \( v^+ \) is proportional to its rate of production, i.e., partial cross section \( \sigma_{v^+} \). Ratios of the partial cross section curves provide a vibrational branching ratio curve which is utilized in identifying resonant features.

### 4.1.1.2 Results

Figure 4.2 shows a portion of the fluorescence spectrum for the \( \text{N}_2\text{O}^+ (A^2\Sigma^+ \rightarrow \chi^2\Pi) \) band system. The fluorescence detection bandwidth is set at 5.2 A. The fluorescence spectrum resolves the vibrational bands of interest originating from vibrational levels \( v^+ = (0,0,0), v^+ = (1,0,0) \), and \( v^+ = (0,0,1) \), and the assignment is consistent with the results from previous studies \([26,27,112]\). Peaks appear as doublets owing to spin-orbital splitting in the ground ionic state of \( \text{N}_2\text{O} \). The total intensity of a transition is obtained by calculating the area under each peak. Relative partial photoionization cross section curves for the \( v^+ = (0,0,0), v^+ = (1,0,0) \), and \( v^+ = (0,0,1) \) levels are
obtained from CIS spectra with $\lambda_R = 3550, 3389, \text{ and } 3464$ A, respectively. The results are shown in Fig. 4.3. The $v^+ = (0,0,0)$ curve is in good agreement with the cross section curve calculated by Braunstein and McKoy [30] for vibrationally unresolved N$_2$O 7σ$^\text{-1}$ photoionization, and all of the CIS curves in Fig. 4.3 are consistent with the previous vibrationally resolved fluorescence studies by our group [27].

Figure 4.2 Portion of the fluorescence spectrum of N$_2$O$^+$ ($A^2\Sigma^+ \rightarrow X^2\Pi$). The fluorescence detection bandwidth is set at 5.2 A. Transitions of interest are labeled according to ref.[112]. The doubling features are due to spin-orbital splitting in the ground ionic state of N$_2$O, not the excited state [N$_2$O$^+(A^2\Sigma^+)$] which is fluorescing.
CIS SPECTRA OF N₂O⁺(A²Σ⁺)

Figure 4.3 Constant ionic state (CIS) spectra for several vibrational levels of N₂O⁺(A²Σ⁺).

Vibrational branching ratio for photoionizing from the ground state to v⁺ = (0,0,0), v⁺ = (1,0,0), and v⁺ = (0,0,1) levels of the A²Σ⁺ state is given by Eq. 3.13. The ratios of Franck-Condon factors are obtained by comparing
the florescence data to the photoelectron spectroscopy data [25]. Hence, vibrational branching ratio curves are generated from ratios of the CIS scans scaled to the photoelectron vibrational branching ratios at 20 eV. The results are shown in Fig. 4.4. The picture emerging from much wider spectral range (E_k ≤ 230 eV) in the current study is very illuminating. Both curves show a minimum at hv_{exc} ≈ 20 eV and an enhancement at ~ 38 eV. The branching ratio curves for

![Graph showing branching ratios for N_2O^+(A^2Σ^+)](image)

Figure 4.4 Vibrational branching ratios for N_2O^+(A^2Σ^+): σ(1,0,0)/σ(0,0,0) and σ(0,0,1)/σ(0,0,0). Note that there is an enhancement around 38 eV in both curves. The σ(1,0,0)/σ(0,0,0) and σ(0,0,1)/σ(0,0,0) curves deviate from Franck-Condon behavior over a broad energy range.
σ(1,0,0)/σ(0,0,0) and σ(0,0,1)/σ(0,0,0) show photon energy dependence over a broad spectral range, and approach the Franck-Condon limit of 0.30 for σ(1,0,0)/σ(0,0,0) and 0.14 for σ(0,0,1)/σ(0,0,0) at hν_{exc} ≈ 200 eV. Current results are in good qualitative agreement with earlier results [25,30], which will be discussed in more detail later. These observations imply a breakdown of the Franck-Condon approximation. Moreover, the branching ratios appear to have a small but significant changes over a broad range, which may come from the influence of Cooper minima.

Figure 4.5 shows current σ(1,0,0)/σ(0,0,0) and σ(0,0,1)/σ(0,0,0) branching ratios for 7σ^{-1} photoionization along with the previous photoelectron and calculated data of Ferrett, et al.[25] and Braunstein and McKoy [30], respectively, within 17 ≤ hν_{exc} ≤ 55 eV range. The agreement for asymmetric stretching [σ(0,0,1)/σ(0,0,0)] branching ratio curves is very good; the overall shape of experimental symmetric stretching [σ(1,0,0)/σ(0,0,0)] curve agrees with the theoretical curve except a shift in the Franck-Condon limit.

Figure 4.6 compares previous fluorescence results by L.A. Kelly [27] with current σ(1,0,0)/σ(0,0,0) and σ(0,0,1)/σ(0,0,0) branching ratios. There is a serious discrepancy in the σ(1,0,0)/σ(0,0,0) curves above 25 eV, resulting from the fact that previous data sets were taken from two different beamlines and scaled to each other, then joined at 25 eV.

The second part of the study focuses on the alternative vibrational mode, i.e., the bending mode. I study this degree of freedom by examining the fluorescence originating from the N₂O⁺[A²Σ^+, v' = (0,1,0)] level. This fluorescence transition is rather weak, restricting data accumulation to photon...
Figure 4.5 Comparison of vibrational branching ratios for \( \text{N}_2\text{O}^+ (\text{A}^2\Sigma^+) \). Top frame is \( \sigma(1,0,0)/\sigma(0,0,0) \); bottom frame is \( \sigma(0,0,1)/\sigma(0,0,0) \). Filled symbols are current data; open symbols are photoelectron data [25]; theory curves from Braunstein and McKoy [30].
Figure 4.6 Comparison of vibrational branching ratios for N$_2$O$^+$(A$^2$Σ$^+$). Upper frame is $\sigma$(1,0,0)/$\sigma$(0,0,0); Lower frame is $\sigma$(0,0,1)/$\sigma$(0,0,0). Filled symbols are our current data; open symbols are old fluorescence data from ref. [27]; solid lines are calculated results from Braunstein and McKoy [30]. Note that there is a serious discrepancy in the $\sigma$(1,0,0)/$\sigma$(0,0,0) curve above 25 eV.
energies below 100 eV. However, even though the energy range is restricted, it is still the first observation for any bending mode over such a broad photon energy range. The previous studies [2,27] were limited to photon energies below 25 eV. Figure 4.7 shows a high resolution fluorescence spectrum ($\Delta \lambda_{fl} = 2.16 \text{ A}$) of the bending excitation [$v^+ = (0,1,0) \rightarrow v'' = (0,1,0)$, $\lambda_{fl} = 3520.8 \text{ A}$] near the $v^+ = (0,0,0) \rightarrow v'' = (0,0,0)$ transition shown in Fig. 4.2. Interpreting the fluorescence from the $v^+ = (0,1,0)$ level requires a note of caution, as previous
studies indicated that ions with bending excitation are created predominantly by photoionization of the neutral molecule with one quantum of vibrational excitation in the $v_2$ mode, i.e., hot band excitation $v_0 = (0,1,0)$ [86,87,113], not $v_0 = (0,0,0)$. Therefore, this branching ratio curve $\sigma(0,1,0)/\sigma(0,0,0)$ can not be compared directly with the other branching ratio curves, because this measurement examines the effects of shape resonant excitation from a vibrationally excited neutral target state. The ratio of fluorescence intensities, which is proportional to the vibrational branching ratio, provides the pseudo-branching ratio profile as a function of excitation energy. (Hereafter, I will refer to this as a branching ratio, even though the meaning is slightly modified from the typical usage of the term.) The CIS curves for $[v^+ = (0,1,0), v^+ = (0,0,0)]$ and resulting branching ratio profile are shown in Fig. 4.8. Two CIS curves are different from each other. An enhancement around 38 eV is apparent in both CIS curves, but it shifts to lower energy in $v^+ = (0,1,0)$ curve. Clearly, the branching ratio profile is photon energy dependent, which provides qualitative insights into the bending ionization dynamics.

4.1.1.3 Discussion

Overall Energy Dependence: In the previous studies [26,27,30], it was found that the vibrational branching ratios show non-Franck-Condon behavior for both stretching vibrational modes; at lower energies especially, the deviations are are much more pronounced in the symmetric mode than in asymmetric mode. Figure 4.5 compares present vibrational branching ratio curves for 7σ⁻¹ photoionization of N₂O with vibrationally resolved calculation by Braunstein and
Figure 4.8 Upper frame: constant-ionic-state spectrum of \( N_2O^+ (A^2\Sigma^+) \) state \( v^+ = (0,1,0) \rightarrow v'' = (0,1,0) \). Middle frame: \( v^+ = (0,0,0) \rightarrow v'' = (0,0,0) \). Lower frame: relative branching ratio profile that is not normalized to photoelectron data, \( \sigma(0,1,0) / \sigma(0,0,0) \).
McKoy [30] and the photoelectron data [25]. The current N$_2$O fluorescence study is complemented by the photoelectron work [25] (open symbol) at the lower photon energy range. The results are in excellent agreement. The most significant feature in the $\sigma(1,0,0)/\sigma(0,0,0)$ branching ratio near the ionization threshold is the strong energy dependence around a photon energy of 20 eV which arises from the $k\sigma$ shape resonance (first shape resonance in the 7$\sigma$ channel). The dip in the calculated branching ratio curve occurs at higher energy than the one we see experimentally. This discrepancy is probably due to inaccurate potentials used in obtaining the vibrational wave functions for the N$_2$O$^+$[30]. In general, the overall shape of current $\sigma(1,0,0)/\sigma(0,0,0)$ curve agrees well with the theoretical results. The non-Franck-Condon behavior also extends to higher energy (see, Fig.4.4), i.e., the $\sigma(1,0,0)/\sigma(0,0,0)$ and $\sigma(0,0,1)/\sigma(0,0,0)$ curves keep rising until they appears to stay constant at energies ~ 200 eV. The value 0.32 for $\sigma(1,0,0)/\sigma(0,0,0)$ is very close to the calculated Franck-Condon limit at 55 eV. Based on the comparisons made in Figs. 4.5 and 4.6, I conclude that the current N$_2$O results have better agreement with the theory than previous fluorescence results.

The behavior exhibited by the branching ratio curves suggests a simple physical interpretation that the resonance trapping occurs over a wider region of space which encompass the whole molecule, and that the resonance position and width depend primarily on the overall length of the molecule. This hypothesis can be justified by considering Fig. 4.1, which shows a sketch of the vibrational motion of the ion in $v^+= (1,0,0)$, $v^+= (0,0,1)$, and $v^+= (0,1,0)$ states. Because the symmetric stretching vibration of N$_2$O ion in $v^+= (1,0,0)$ changes the overall
molecular "length" [compared to the \( v^+ = (0,0,0) \)], therefore, the barrier to photoelectron trapping. In contrast, the asymmetric stretch mode does not appreciably change the "length" of the molecule, and hence, the cross section curve for this level is almost the same as that for the \( v^+ = (0,0,0) \) level. The relatively flat \( \sigma(0,0,1)/\sigma(0,0,0) \) curve (bottom frame of Fig. 4.5) supports this hypothesis, in agreement with what is calculated by independent \textit{ab initio} Schwinger variation method [30] (solid line). The key point here is that the strong non-FC behavior results from a dependence of the electronic-dipole matrix on alternative molecular configurations for the \( N_2O^+(A^2\Sigma^+) \) ion.

In addition, we see a new feature in the current study, an enhancement centered at \( \sim 38 \text{ eV} \) (in Fig. 4.3 and Fig. 4.4), which was not observed in previous study, coinciding with the second shape resonance in the \( 7\sigma \rightarrow k\sigma \) photoionization channel calculated by Braunstein and McKoy [51]. Carlson \textit{et al.} assigned this peak as a \( k\sigma \) shape resonance on the basis of a dip in the photoelectron asymmetry parameter as well as the observed cross section enhancement [107]. While the dip in \( \beta \) is most likely due to the \( k\sigma \) shape resonance, Braunstein and McKoy [51] has suggested that this enhancement is due to both resonant and nonresonant contributions. The electron ejected from a \( 7\sigma \) orbital can have either \( k\sigma \) or \( k\pi \) symmetry, and the calculation suggested that the enhancement in the cross section is due mainly to the increasing \textit{nonresonant} contribution of the \( k\pi \) channel [51]. However, there is still a significant contribution from the \( k\sigma \) channel even though the \( k\pi \) channel dominates above 30 eV. Since shape resonances cover broad energy ranges (typically > 15 eV), L.A. Kelly \textit{et al.} [27] suggested that the cross section is very likely enhanced by
the high or low energy $k\sigma$ resonances or the combination of both in conjunction with the nonresonant $k\pi$ contribution in that energy region. The enhancement shown in the current vibrational branching ratio data at $\sim 38$ eV supports the argument that there are resonant contributions involved in that energy region.

The most interesting features observed in current study are the wide-ranging excursions from Franck-Condon behavior as shown in Fig.4.4. The deviation is larger for $\sigma(1,0,0)/\sigma(0,0,0)$ than for $\sigma(0,0,1)/\sigma(0,0,0)$ curve, extending a broad energy range of more than 200 eV. Similar behaviors have been observed in $N_2 2\sigma_u^{-1}$ photoionization [114], and the source of the Franck-Condon breakdown was interpreted as a strong dependence of Cooper minima (occurring at $h\nu_{exc} \approx 120$ eV) on internuclear separation $R$. Cooper minima originate from a change in sign of the transition dipole matrix element, so that the matrix element goes through zero [115]. While shape resonances and Cooper minima cause coupling between electronic and vibrational degrees of freedom, it is necessary to examine the mechanisms for Franck-Condon breakdown. In resonant excitation, either shape resonance, or autoionization, the eigenphase sum goes through $\pi$, and the cross section goes through a local maximum or minimum. Cooper minima are nonresonant, i.e., the eigenphase sum does not go through $\pi$ in the vicinity of the Cooper minimum. Instead, the cross section exhibits an inflection. Cooper minima are ubiquitous for atomic and molecular systems [115]. For polyatomic molecular systems, the effects of Cooper minima on photoelectron angular distributions are well documented [116,117]. However, the influence of Cooper minima on molecular vibration over a large spectral
range has never been explored, and the current \( N_2O \) 7\( \sigma^- \) results might form a strong case for theoretical study.

There are two likely mechanisms which can contribute to the non-FC behavior (Fig. 4.4), and both may play a role here. First, there is a strong shape resonance which is responsible for the minimum at 20 eV, resulting in the Franck-Condon breakdown in lower energy. Second, the high energy non-FC behavior over a broader range than any previous studied resonant mechanisms is likely relating to Cooper minima. The non-symmetric polyatomic molecule \( N_2O \) makes the transition dipole matrix element much more complicated than that of diatomic molecule \( N_2 \), so that further theoretical calculations are needed to clarify the nature of the wide-ranging excursions shown in Fig. 4.4.

Bending Vibration: The fluorescence from the \( N_2O^+(A^2\Sigma^+) \) with bending excitation is presented in Fig. 4.8, \( h\nu_{exc} = 20 \) to 100 eV. Previous studies [86,87] indicated that ions with bending excitation are created primarily by the photoionization of vibrationally hot \( [v_0=(0,1,0)] \) \( N_2O \). Similar hot-band excitation is not expected to be nearly as prevalent for either of the stretching modes since their higher vibrational frequencies preclude significant population at the experimental temperature. The Boltzman factors of three vibrational states for ground state of neutral \( N_2O \) are compared in Table 4.1.

The most significant feature in the branching ratio (bottom frame of Fig. 4.8) is its strong energy dependence: there is a pronounced minimum around 20 eV which arises from the first \( k\sigma \) shape resonance seen in the result of Fig. 4.5; and a broad enhancement around 38 eV which has been interpreted as
Table 4.1. Boltzman factors for N\textsubscript{2}O (X\textsuperscript{1}Σ\textsuperscript{+}) at room temperature\textsuperscript{(a)}

<table>
<thead>
<tr>
<th>Vibrational State</th>
<th>(\text{Exp}{-E((n_1,n_2,n_3))/KT}\textsuperscript{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>1</td>
</tr>
<tr>
<td>(1,0,0)</td>
<td>(1.621 \times 10^{-3})</td>
</tr>
<tr>
<td>(0,1,0)</td>
<td>(5.266 \times 10^{-2})</td>
</tr>
<tr>
<td>(0,0,1)</td>
<td>(1.483 \times 10^{-5})</td>
</tr>
</tbody>
</table>

(a). At room temperature, \(KT = 200 \text{ cm}^{-1}\) [81,108].

(b). \(v_1 = 1284.9 \text{ cm}^{-1}\), \(v_2 = 588.77 \text{ cm}^{-1}\), \(v_3 = 2223.76 \text{ cm}^{-1}\) from ref. [81,108].

nonresonant but arises from the usual energy dependence of the \(k\pi\) contribution; and finally reaches the FC limit (0.053). The results provide a surprising implication, namely, that the resonant excitation of the bending vibration becomes dominant in cross section curve at \(\sim 38 \text{ eV}\) region and, hence, shows strong non-FC effects in the vibrational branching ratio. As is discussed in last section, the origin of this higher energy enhancement is less certain. Our current data for the bending excitation suggest that this higher energy enhancement can be mainly attributed to the contribution of the lower energy shape resonance. It is very likely that the shape resonance peaks to lower photon energy (< 20 eV) in the (0,1,0) CIS, in other words, we just observed the tail of that resonance at 20 eV. Furthermore, the CIS curve of (0,1,0) displays a wider profile at \(\sim 38 \text{ eV}\) region than the (0,0,0) CIS does. It is the different resonance width that contributes to the dramatic deviation in the branching ratio curve at that energy region.
These results are surprising because one usually assumes that the 
$\sigma(0,1,0)/\sigma(0,0,0)$ and $\sigma(0,0,1)/\sigma(0,0,0)$ curves are somewhat similar based on 
the argument that the overall molecular length does not change appreciably with 
bending excitation for either the ground state neutral molecule or the A state of 
the ion [108]. Purely for suggestive reasons, three vibrational branching ratios, 
in 20-60 eV region, are compared and shown in Fig.4.9. One question arises 
naturally why the shape resonant excitation affects the vibrational behavior so 
dramatically in the bending mode than in the stretching modes. There are no 
calculations are available in this vibrational channel to give some physical 
insights. However, one might interpret those differences by considering 
molecular geometry changes: bending vibration changes the *width* of the "box", 
which is trapping the ejected photoelectron, rather than the *length* of the "box" 
by stretching vibrations.

Although this interpretation is suggestive, the results themselves provide 
an interesting example of polyatomic shape resonant behavior. Using the 
vibrational motion as a probe of internuclear distance provides qualitative 
information on the nature of the trapping site of the resonant state in a polyatomic 
molecule. In particular, there is the possibility probing more details of the spatial 
character of the continuum wave function by probing bending vibrations than is 
possible with stretching vibrations.

### 4.1.1.4 Conclusion

Vibrationally resolved photoionization data have been obtained for 
$\text{N}_2\text{O}^+\text{(A}^2\Sigma^+\text{)}$ in the photon energy range $20 \leq h\nu_{\text{exc}} \leq 250$ eV. Its associated
vibrational levels: (0,0,0), (1,0,0), (0,0,1), and bending mode (0,1,0) are fully studied. The comparison between vibrational branching ratios for symmetric

![Graph](image)

**Figure 4.9** Comparison of vibrational branching ratios for N$_2$O$^+$ ($A^2\Sigma^+$) state as a guide for discussion. Upper frame and middle frame: branching ratios are normalized to the photoelectron data. Lower frame: vibrational branching ratios are not normalized to photoelectron measurement.
versus asymmetric stretching motion over a broad spectral range provides qualitative insights into the extent of the photoelectron trapping for the shape resonant photoionization. Particularly, study of bending mode provides more information on how vibrational motion is affected by the spatial characteristics of shape resonant state. These experimental results, in conjunction with the calculations and photoelectron data, further support the contention that shape resonance trapping of the photoelectron is relatively delocalized over the molecular length. The nature of the 38 eV enhancement is clarified in current study, and the results have better agreement with the theory for the $\sigma(1,0,0)/\sigma(0,0,0)$ branching ratio above 25 eV. The current bending mode results demonstrate the necessity for the theoretical calculations to elucidate this new type of strong non-Franck-Condon behavior. Our investigations illustrate the utility of vibrationally resolved measurements as a probe of fundamental aspects of molecular scattering phenomena.

4.1.2 $3\sigma_u^{-1}$ Photoionization of CO$_2$

4.1.2.1 Introduction

CO$_2$ was chosen as the target system in this study for several reasons. First, vibrationally resolved data already exist for the valence isoelectronic systems of N$_2$O [26,27,25] and CS$_2$ [118]. It is useful to study analogous systems for discerning the trends and differences in the ionization dynamics over a broad spectral region. Second, CO$_2$ is also a linear triatomic molecule and it is the simplest extension beyond diatomic molecules. Third, CO$_2$ is different from
N₂O in the sense that CO₂ is a symmetrical molecule (O-C-O), and this might influence the vibrational bending motion differently and hence the ionization dynamics.

The ground state electronic configuration of CO₂ can be written as \( \text{KKK}(3\sigma_g)^2(2\pi_u)^2(4\pi_g)^2(3\rho_u)^2(1\pi_u)^4(1\pi_g)^4 \ X^1\Sigma_g^+ \)\[^{[108]}\]. The photoionization channels lead to the four lowest states of CO₂⁺, which are the \((1\pi_g)^{-1} \ X^2\Pi_g\) state obtained by ionizing an electron from the \(1\pi_g\) orbital with a vertical ionization potential (IP) of 13.8 eV; the \((1\pi_u)^{-1} \ A^2\Pi_u\) state with an IP of 17.7 eV; the \((3\sigma_u)^{-1} \ B^2\Sigma_u^+\) state with an IP of 18.2 eV; and the \((4\sigma_g)^{-1} \ C^2\Sigma_g^+\) state with an IP of 19.4 eV \[^{[108]}\]. As in N₂O, there are three normal vibrational modes associated with the \(\nu_1(\sigma_g^+)\) symmetric stretching mode; \(\nu_2(\pi_u)\) bending mode (degenerate); and \(\nu_3(\sigma_u^+)\) asymmetric stretching mode \[^{[119]}\]. The bending mode is symmetry forbidden in the absence of vibronic coupling.

Of particular interest is the theoretically well-characterized shape resonance \((4\sigma_g \rightarrow k\sigma_u)\) \[^{[120-122]}\]. There have been several calculations \[^{[122-124]}\] on differential and total cross sections for shape resonant photoionization leading to \(X^2\Pi_g, A^2\Pi_u, B^2\Sigma_u^+\), and \(C^2\Sigma_g^+\) states of CO₂⁺ as well as for oxygen and carbon K-shell photoionization. Those calculated results were compared with experimental data, and there are two major disagreements. The first is that the experiments did not reveal the computed resonant enhancement for the \(4\sigma_g^{-1}\) partial photoionization cross section. However, the experimentally determined asymmetry parameters of Carlson et al.\[^{[125]}\] do support the existence and the predicted position of this shape resonance. The second disagreement is that the experimental cross section of \(B^2\Sigma_u^+\) state exhibits a peak at photon energy 21 eV,
which is not obtained in the calculation by Lucchese and McKoy [122]. Moreover, the recent calculation by Lucchese predicted that there is an interchannel coupling effect between the shape resonant $4\sigma_{g} \rightarrow k\sigma_{u}$ ionization channel of CO$_2$ on the asymmetry parameter in the $3\sigma_{u} \rightarrow k\sigma_{g}$ channel around $h\gamma_{exc} \approx 40$ eV [124]. For these reasons, we chose the CO$_2^+$(B$^2\Sigma_u^+$) state to test the effects due to interchannel coupling. Also, we have included observations of the bending mode behavior for comparison with the N$_2$O results.

Experimentally, we use vibrationally resolved fluorescence data from CO$_2^+$(B$^2\Sigma_u^+$) in an effort to elucidate fundamental aspects of shape resonance mediated continuum channel coupling. The resonant behavior of CO$_2^+$(B$^2\Sigma_u^+$) is probed by monitoring vibrationally resolved fluorescence from the photoion with synchrotron radiation excitation, and then generate vibrational branching ratio as a function of photon energy. The excitation/detection sequence for the present study is illustrated by Eq. 4.2,

$$\text{CO}_2[X^1\Sigma_g^+, v_0=(0,0,0)] + h\gamma_{exc} \rightarrow \text{CO}_2^+[B^2\Sigma_u^+, v^+ = (n_1^+, n_2^+, n_3^+)] + e^- \downarrow \text{CO}_2^+[X^2\Pi_g, v''=(n_1'', n_2'', n_3'')] + h\gamma_{v'v''}$$

(4.2)

CO$_2$ molecules in the ground state ($X^1\Sigma_g^+$) are photoionized to alternative vibrational levels of the ion CO$_2^+$(B$^2\Sigma_u^+$), and then undergo radiative decay to the ionic ground state ($X^2\Pi_g$). In the current study, the fluorescence originating
from the \( v^+ = (0,0,0) \) and \( v^+ = (0,1,0) \) levels of \( \text{CO}_2^+ (B^2\Sigma_u^+) \) are measured over the photon energy range \( 20 \leq h\nu_{\text{exc}} \leq 200 \text{ eV} \).

### 4.1.2.2 Results

Figure 4.10 shows a \( \text{CO}_2^+ (B^2\Sigma_u^+ \rightarrow X^2\Pi_g) \) fluorescence spectrum around 2860-2910 Å region. The fluorescence detection bandwidth is set at 2 Å. The transitions of interest are those originating from \( v^+ = (0,0,0) \) and \( v^+ = (0,1,0) \), and the spectroscopic assignments are based on earlier work [113]. Peaks appear as doublets owing to spin-orbital splitting in the ground ionic state. The integrated area of each peak is proportional to the cross section for the production of the vibrational level from which the transition originates. A plot of the fluorescence intensity as a function of excitation photon energy generates the relative CIS spectrum for that vibrational level. In the same vein, the ratio of these two CIS spectra, i.e., \( \sigma(0,1,0)/\sigma(0,0,0) \), yields the vibrational branching ratio profile. Figures 4.11a and 4.11b show CIS spectra for the levels \( v^+ = (0,0,0) \) and \( v^+ = (0,1,0) \) with \( \lambda_{\text{fl}} = 2895 \text{ Å, 2874 Å} \), respectively.

There is a resonant enhancement in the CIS curve at approximately 21 eV which is characterized as an autoionization of Rydberg levels converging to higher-lying ionic states [126]. Around 38 eV, another resonant enhancement is observed in the CIS curves which is very likely the interchannel coupling enhancement that we wish to study. Therefore, there are two resonance features observed in 20–50 eV range; an autoionizing resonance at \( h\nu_{\text{exc}} \approx 21 \text{ eV} \), and an interchannel coupling enhancement at \( h\nu_{\text{exc}} \approx 40 \text{ eV} \). Our CIS curve for \( v^+ = (0,0,0) \) agrees well with previous vibrationally unresolved calculations [127].
and the experimental data [127-129], which are compared in Fig. 4.12. Their data are normalized to the current data at 30 eV. Figure 4.11(c) illustrates the vibrational branching ratio profile \( \sigma(0,1,0)/\sigma(0,0,0) \). Evidently, the vibrational branching ratio is photon energy dependent indicating the Franck-Condon breakdown, and the current vibrationally resolved data provide additional qualitative insights into the molecular scattering dynamics.

\[ \text{CO}_2^+ (B^2\Sigma_u^+ \rightarrow X^2\Pi_g) \]

\[ h\nu_{\text{exc}} = 40 \text{ eV} \]

\[ (0,0,0) \rightarrow (0,0,0) \]

\[ (0,1,0) \rightarrow (0,1,0) \]

\[ x8 \]

Figure 4.10 Portion of the fluorescence spectrum of \( \text{CO}_2^+ \) \( (B^2\Sigma_u^+ \rightarrow X^2\Pi_g) \). The fluorescence bandwidth is set at 2 Å. Transitions of interest are labeled according to ref. [113]. The doublets are due to spin-orbital splitting in the ground ionic state, not the excited state \([\text{CO}_2^+ (B^2\Sigma_u^+)]\).

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Figure 4.11 (a): constant-ionic-state spectrum of \( \text{CO}_2^+ (B^2\Sigma_u^+) \) state \( v^+ = (0,0,0) \rightarrow v'' = (0,0,0) \) (b): \( v^+ = (0,1,0) \rightarrow v'' = (0,1,0) \) (c): relative branching ratio curve that is not normalized, \( \sigma(0,1,0)/\sigma(0,0,0) \).
4.1.2.3 Discussion

Lower Energy Region: Current experimental results are in good agreement with the theoretical calculations by Lucchese and McKoy employing single-center frozen-core Hartree-Fock (FCHF) approximation [127] (Fig. 4.12). The resonant enhancements in the cross section are apparent in both the experimental and theoretical curves at \( h\nu_{\text{exc}} \approx 21 \text{ eV} \); there is an excellent agreement for the
magnitude of the resonance. Figure 4.12 compares our cross sections to the experimental fluorescence data of Carlson et al. [128] and the photoelectron cross sections obtained by taking the total A+B cross sections of Brion and Tan [129] and using the A/B ratios of Samson and Gardner [129]. The agreement is reasonably good with the fluorescence measurement data, whereas there is a serious disagreement with the photoelectron data at ~ 21 eV. This disagreement seems to indicate that at $h\nu_{\text{exc}} \approx 20$ eV, there is an autoionization. An earlier study has shown that there are strong final state correlation effects in the inner valence photoionization of CO$_2$ [58]. These correlation effects mix single hole states, two hole-one particle states, and higher order hole-particle combination states to bring about the breakdown of the single particle model. The lowest multielectron ionic state of CO$_2$ is located at 23 eV and has been characterized by Domcke et al. [58] as being dominated by the $\left(1\pi_g\right)^2(2\pi_u)$ configuration. This autoionization enhancement would be analogous to the enhancement due to the $C^2\Sigma_u^+$ state in the photoionization cross section of N$_2$ [130].

It has been suggested [129] that there is a crossover mechanism involved in the autoionization region: a large fraction of the molecules which are initially in the B state crossover to the A state before the molecule ion fluoresces. Because these ionic states are separated in energy by less than 1 eV, strong perturbations occur between the ionic states and between the corresponding Rydberg series. Since the agreement between the fluorescence data and photoelectron data is much better in the 40.8 eV than in the 21 eV region, it was speculated [127] that the mechanism must depend on the photon energy and in particular the presence of autoionization must strongly effect the crossover rate.
The calculations [124] show that the effect of initial-state correlation on the enhancement in the $3\sigma_u \rightarrow k\sigma_g$ cross section is to increase the difference between length and velocity forms of the cross section rather than to bring them together in the shape resonance case. Thus, it seems that the $k\sigma_g$ ionization continuum channel is being affected by a resonant process which is qualitatively different from the usual shape resonances.

Based on all these facts, it appears that the feature at 21 eV is the autoionization. This is further supported by the narrow width observed in current vibrationally resolved partial ionization cross section curve (see, Fig.4.11), which is consistent with an autoionization resonance feature. It also shows in the branching ratio curve as a deep dip. Therefore, I conclude that the lower energy feature ($h\nu_{exc} \approx 21\text{eV}$) is the previously identified autoionization, and the current results supplement the past work by probing the vibrationally resolved behavior.

Higher Energy Region: While the assignment of the lower energy feature as an autoionization is indirect, the origin of the higher energy enhancement is relatively straightforward. In the previous studies of CO$_2$ by Padial et al.[123], the theoretical curve for the CO$_2^+$(B$^2\Sigma_u^+$) photoionization cross section shows an enhancement in the energy region of 40 eV, and the (e, 2e) [129] and fluorescence data [128] are consistent with the calculations. They attributed this broad enhancement at $\sim 40$ eV due to the $3\sigma_u \rightarrow k\pi_g$ nonresonant contribution, which contains a d-orbital contribution. However, the recent calculations by Lucchese [124] indicate that in the coupled-channel approximation, the shape resonance in the $4\sigma_g \rightarrow k\sigma_u$ channel ($h\nu_{exc} \approx 40 \text{eV}$) is found to modify the cross
sections and asymmetry parameters in the other channels, with the largest effect being in the \((3\sigma_u)^{-1}\) ionization channel.

It is known that, in addition to modifying the total and differential cross sections in a resonant channel, interchannel coupling has a pronounced effect on other channels at energies near the position of the resonance [131-133]. Let's look the calculations of single channel, three channel, and four channel coupling by Tamm-Dancoff approximation (TDA) [124], and compare them with current vibrationally resolved cross section curve as shown in Fig. 4.13. We can see that the three channel result (including the coupling to the \(1\pi_u \rightarrow k\pi_g\) channel) increases the total cross section in better agreement with the experimental data in the higher energy region than in the lower energy region due to the interchannel coupling to the resonant \((4\sigma_g)^{-1}\) channel at the energy region. It was found that in the asymmetry parameters for the \((3\sigma_u)^{-1}\) channel, there is a much more dramatic effect near 41 eV (see Fig. 6 in ref [124]). The position of the dip in the \(\beta\) curve at 41 eV is in good agreement with our experimental data showing the enhancement at 41 eV. The disagreement with the experimental data near 20 eV indicates that for the theory to yield more accurate results, both target correlation effects and multielectron ion states must be included in the calculation. I emphasize that our current data are in excellent agreement with FCHF calculations both in low and high energy region [127].

Naturally, the effect of coupling between vibrational and electronic motion can be expected to be important in the photoionization cross sections when the photon energy is close to a resonance energy. The result in Fig. 4.11(c) for the \(\sigma(0,1,0)/\sigma(0,0,0)\) branching ratio shows a strong deviation at \(h\nu_{exc} \approx 38\)
eV, indicating that $4\sigma_g \to k\sigma_u$ shape resonance does strongly affect this $(3\sigma_u)^{-1}$ channel vibrational branching ratio, which supports the theoretical prediction.

Vibrational Bending Motion: Figure 4.11 shows the photoionization cross section curves and the vibrational branching ratio curve for the bending excitation of $\text{CO}_2^+(B^2\Sigma_u^+)$. The branching ratio profile shows a strong deviation centered at

![Graph showing photoionization cross section curves and vibrational branching ratio for $\text{CO}_2^+(B^2\Sigma_u^+)$]

**Figure 4.13** Comparison of different theoretical cross sections and our present data for the $\text{CO}_2^+(B^2\Sigma_u^+)$.

The data are normalized to the FCHF calculation [127] at 30 eV. Our measurements are in good agreement with single-center FCHF results; it is in reasonably agreement with three-channel calculations in the higher energy region.
~ 38 eV owing to the interchannel coupled resonance. The origin of the dip at ~
58 eV is unknown. It can be seen from CIS curves that the peak positions of
38 eV enhancement are nearly the same, but the width is narrower in \( v^+ = (0, 1, 0) \)
than in \( v^+ = (0, 0, 0) \) curve. It is the width difference that causes the broad
excursion (~ 20 eV) in the branching ratio curve. The large excursion further
supports the assertion that the observed feature is due to a shape resonance, and
in this case, an interchannel-coupled shape resonance. The vibrational branching
ratio shows significant non-Franck-Condon behavior, but calculations are not yet
available for comparison.

In the previous \( \text{N}_2\text{O} \) studies, the data were readily amenable to the
interpretation as alternative vibrational modes were accessible (symmetric stretch,
bending, asymmetric stretch). In the present study, only the \( v_2 \) vibrational mode
has sufficient intensity to be probed in the ~ 2890 Å fluorescence wavelength
range of interest to avoid the A and B state mixtures above 3000 Å.

In order to glean physical insights into the dependence of shape resonant
behavior on bending vibration, it is useful to compare the analogous molecular
systems. Figure 4.14 compares bending vibrational branching ratios from studies
on \( \text{N}_2\text{O} \) with the present results on \( \text{CO}_2 \). The top frame shows the
\( \sigma(0, 1, 0)/\sigma(0, 0, 0) \) ratio of \( \text{CO}_2 \) results from Fig.4.11(c). The bottom frame
displays the analogous \( \sigma(0, 1, 0)/\sigma(0, 0, 0) \) ratio for the \( 7\sigma^{-1} \) photoionization of
\( \text{N}_2\text{O} \). Coincidentally, there is a broad enhancement in both branching ratio curves
around 38 eV, but their origins are different, as discussed above. For \( \text{N}_2\text{O} \), the
first shape resonance (\( h\nu_{\text{exc}} \approx 20 \) eV) causes the vibrational branching ratio to
change by more than a factor of two. The tail of that shape resonance contributes
to the broad enhancement around the 38 eV. It is obvious that the deviations of vibrational branching ratios in CO$_2$ are comparatively small. These results imply that shape resonant ionization dynamics might be sensitive to changes in the molecular symmetry.

Figure 4.14 Comparison of bending mode $v^+ = (0,1,0) \rightarrow v'' = (0,1,0)$ vibrational branching ratios for N$_2$O$^+$($A^2\Sigma^+$) and CO$_2$$^+$($B^2\Sigma_u^+$) as a guide for discussion.
The behavior of shape resonant responses to bending motion can be rationalized as follows. First, the bending motion reduces the symmetries of $\text{N}_2\text{O (C}_\infty\text{)}$ and $\text{CO}_2 (D_{\alpha h})$, and mixes the $C_{\infty v}$ and the $D_{\alpha h}$ irreducible representations within $\text{N}_2\text{O}$ and $\text{CO}_2$, respectively [134]. These mixings lead to the coupling of partial waves (both $l$ and $m$ values) which are not coupled by the symmetric stretch motion. Second, bending generates a dipole moment, therefore, there might be coupling between the different symmetry continuum electrons ($k\pi$, $k\sigma$). Both of these couplings are expected to have a pronounced consequences on the photoionization cross sections in these channels with shape resonance features.

Although $\text{N}_2\text{O}$ and $\text{CO}_2$ are linear triatomics that are isoelectronic, $\text{N}_2\text{O}$ has lower symmetry in contrast to $\text{CO}_2$. The lowered symmetry necessarily increases the complications of basis functions on the center $\text{N}$ atom and side $\text{N}$ atom in contrast to different center $\text{C}$ atom and side $\text{O}$ atoms. On this basis, we propose a hypothesis that shape resonance is sensitive to internuclear configurations and molecular symmetry. $\text{CS}_2$ (linear, symmetric, triatomic), thus, will be ideal candidate to test this hypothesis. As a concluding remark, I note that the current results underscore the need for theoretical studies into the influence of bending motion on shape resonances, as the results cannot be interpreted without a picture of the spatial characteristics of the resonant continuum wave function.

4.1.2.4 Conclusion

Vibrationally resolved fluorescence data have been obtained for $\text{CO}_2(B^2\Sigma_u^+)\text{ photoionization from } 20 \leq h\nu_{\text{exc}} \leq 200 \text{ eV. The CIS spectra for the}
vibrational levels \( v^+ = (0,0,0) \) and \( v^+ = (0,1,0) \) of \( \text{CO}_2^+ (B^2\Sigma_u^+) \) show two resonant features, one at \( h\nu_{\text{exc}} \approx 21 \text{ eV} \) and the other at \( h\nu_{\text{exc}} \approx 40 \text{ eV} \). The low energy resonant feature is interpreted as an autoionization based on the current experimental data; the high energy enhancement is consistent with a previous calculated continuum channel-coupled \( 4\sigma_g^{-1} \) shape resonance. Comparison with the FCHF calculations by Lucchese [127] shows excellent agreement for the cross sections both in low and high energy regions. The comparison between \( \text{CO}_2 \) and \( \text{N}_2\text{O} \) for the bending vibrational branching ratios has the potential of stimulating theory in new directions, and provides qualitative insights into the underlying nature of continuum resonances. We hope that the current studies on \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) will provide additional impetus for characterizing and clarifying the bending vibration in molecular shape resonant photoionization.

4.2 Dissociative Photoionization Dynamics

Vibrationally resolved studies of fragment distributions following photoionization can provide significant insights into the underlying dynamics of dissociative photoionization. In dissociative photoionization, the collision complex \([4,15,16]\) consists of photoelectron(s) and an ion core. Determination of the final state distributions of the photoionization products opens a window on the electronic and nuclear motion of the collision complex responsible for the asymptotic fragment distributions.
Historically, there have been many studies of photodissociative ionization. Of course, the initial step, i.e., the photoionization process, can be probed with photoelectron spectroscopy. However, to determine the subsequent fate of an energetic molecular ion (e.g. whether it predissociates into a fragment ion plus a neutral), coincidence measurements have been found to be extremely helpful [135-139]. Many recent advances have been achieved via combination with tunable intense synchrotron radiation and coincidence measurements [140]. In Photoion-Photoion coincidence (PIPICO) technique, the two ions are detected using a single time-of-flight (TOF) tube and the time difference $\Delta t$ between their TOF is determined. Fragment ions are identified and their kinetic energies of dissociation are obtained by comparing experimental PIPICO curves with simulated ones. Photoion-fluorescence coincidence (PIFCO) [84] allows absolute distinction between ionic and neutral processes, however, only the total fluorescence yields can be measured. Detailed information about a individual fragment is lost. Photoelectron-photoelectron coincidence spectroscopy (PEPECO) [140] with energy analysis of both electrons is the primary means of investigating the mechanism of double photoionization. More recently, the technique of photoelectron-photoion-photoion coincidence (PEPIPICO) has been developed. This method is a triple coincidence technique in which two mass-analyzed ions are detected in coincidence with an electron [140]. This technique ascertains the absolute TOF of each fragment ion, allowing not only unambiguous identification of the ion pairs but also giving additional information on the other uncharged fragments that may be created. This work has made valuable contributions to our knowledge of double ionization of molecules and their
consequences. Overall, a major advantage demonstrated in all these studies is that coincidence measurement can detect many reaction products in time correlated fashion to elucidate the formation of fragment species, their decay pathways, kinetic energy releases, angular distributions, and eventually the dissociation dynamics. While PIPICO and PEPIPICO offer the powerful possibilities of studying dissociative single and double ionizations, there are some limitations (e.g. they can not distinguish two species having same m/e ratios).

While there have been widespread and successful efforts to investigate process of dissociative photoionization using various coincidence methods coupled with synchrotron radiation [141-145], work to date has been focused on the understanding of the branching ratios to the various decay channels, the absolute rate of decay, and the energy partitioning among the product channels near threshold region. A primary drawback is that there is frequently little, if any, information on the internal energy distributions of the fragments. This is where my contribution fills a gap, as it is possible to ascertain information on the internal energies of the fragments via their dispersed emissions. Previous studies were limited to total fluorescence measurements because of excitation flux limitations, which prevented detailed investigations of dissociative photoionization [84,146]. Therefore, application of a dispersed fluorescence technique to individual fragment is necessary to obtain partial cross sections in the dissociative photoionization processes.

Compared with coincidence techniques, dispersed fluorescence spectroscopy coupled with SR offers several advantages. First, dispersed fluorescence spectroscopy provides a signature of the dissociation product, and
can thus be used to identify ionic fragments unambiguously. Secondly, and most importantly, it can provide information about the vibrational and rotational energy deposition into a fragment. That is complementary to coincidence methods. Thirdly, variable excitation energy permits the study of dissociative photoionization at and within the spectral features of interest. An excitation yield curve for a specific ionic fragment can be generated from the fluorescence spectra extending from the dissociation threshold to higher energy range. One can expect to observe peaks corresponding to various dissociative ionization channels. In this respect, this method provides a sensitive and valuable tool to understand the dissociative ionization and double ionization processes at the energies where these processes become significant.

Finally, earlier studies (discussed in section 4.1) demonstrated the utility of dispersed fluorescence detection for probing the Franck-Condon breakdown in shape resonant photoionization dynamics of polyatomic molecules. Moreover, those studies highlighted the important advantages of fluorescence techniques including sensitivity, resolution and uniform collection efficiency. The current study demonstrates an additional advantage, namely, studies to inner-valence region can reveal rich information about excited parent ionic states, i.e., ionic satellite states and doubly ionized states, and shape resonance effects in final two-hole-one-particle ionization channels [147].

4.2.1 N₂O Dissociation

4.2.1.1 Introduction

I present results from measurements of vibrationally resolved dispersed fluorescence from an ionic fragment, N₂⁺(B²Σ⁺ →X²Σ⁺), which is produced
in the dissociative photoionization of N2O. Particularly, these studies probe
inner-valence and higher energy regions. The purpose of the present investigation
is to obtain information about the internal energy deposition into the fragment
N2+, which was not obtained in previous studies [148,149]. The results which
follow demonstrate the utility of examining the final state distribution of ionic
fragment N2+(B2Σu+) over a broad energy region. In particular, such
measurements clarify the roles of alternative dissociation channels.

Fluorescence spectra are obtained in the excitation energy range
20 ≤ hv_{exc} ≤ 150 eV. The specific excitation/decay processes addressed can be
illustrated by Eq. 4.3 (a),(b),(c).

\[
\begin{align*}
N_2O[X^1Σ^+, v_o=0] + hv &\rightarrow N_2^+[B^2Σ_u^+, v^+=0] + O + e^- \quad h\nu \leq 22 \text{ eV} \quad (4.3a) \\
&\rightarrow N_2^+[B^2Σ_u^+, v^+=0] + O^+ + 2e^- \quad 40 \leq h\nu \text{ eV} \quad (4.3b) \\
N_2^+[B^2Σ_u^+, v^+=0] &\rightarrow N_2^+[X^2Σ_g^+, v''=0] + h\nu_{v'+v''} \quad (4.3c)
\end{align*}
\]

No vibrationally excited fragments N2+(B2Σu+) were observed, so we monitor
vibrationally resolved fluorescence from the ground vibrational level of
N2+(B2Σu+, v+=0) while varying the excitation energy. When the excitation
energy less than 22 eV, ground state N2O molecules are photoionized to
alternative excited states A, B, C of N2O+ ions and then undergo radiative decay
(not shown here) or predissociate into N2+(B) and neutral O; when the energy is
greater than \( \sim 40 \) eV, the dissociative double ionization occurs. From 22 eV to 40 eV (inner valence range), electron correlation effects play a dominate role so that the excitation and decay mechanisms are unclear. Here, \( v^+ \) and \( v^- \) denote vibrational levels of the excited electronic state (\( B^2\Sigma_u^+ \)) and the ground electronic state (\( X^2\Sigma_g^+ \)) of \( N_2^+ \), respectively. The fluorescence intensity is proportional to the cross section of the level from which the fluorescence originates and can be used to generate corresponding excitation spectra.

4.2.1.2 Results

An emission spectrum of \( N_2O^+(A^2\Sigma^+ \rightarrow X^2\Pi) \) in the broad wavelength range 3200 - 4200Å is shown in Fig.4.15, obtained at photon energy \( h\nu_{exc} = 50 \) eV. Figure 4.16 shows the portion of Fig. 4.15 for fragment \( N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+) \) relevant to the present study. The detection resolution was 5 Å. Those bands consist of pairs of subbands with almost equal intensity owing to spin-orbit splitting of the ground state of the molecular ion.

The most prominent emission originates from the ground vibrational level of \( N_2O^+(A^2\Sigma^+) \) state \((0,0,0)\); weaker emissions from the \((1,0,0)\), \((0,1,0)\), \((0,0,1)\) are observed. The results are in excellent agreement with our previous photoionization study [112]. The intensity of \( N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+) \) transition is about 17% of the transition for \( N_2O^+[A^2\Sigma^+ , v^+ = (0,0,0) \rightarrow X^2\Pi^+ , v^- = (0,0,0)] \). \( N_2O^+ \) dissociates into \( NO^+, N_2^+, N^+, \) and \( O^+ \) ionic fragments and assorted neutral fragments. Table 4.II lists the several lowest dissociation limits relative to electronic states of \( N_2O^+ \) at energy range 12-22 eV. The energies of \( N_2O^+ \) and its fragments shown are in the lowest vibrational levels. The dissociations of
Figure 4.15 Fluorescence spectrum of $N_2O^+(A^2\Sigma^+ \rightarrow X^2\Pi)$ over a broad spatial range. The fluorescence detection bandwidth is set at 5 A. The transition from the fragment $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ is labeled.

$N_2O^+(B)$ and $N_2O^+(C)$ states have many outgoing channels as the correlation diagram of Lorquet and Cadet [150] indicates. All must be predissociative, since both the $N_2O^+(B)$ and $N_2O^+(C)$ bands in the PES have resolved vibrational structures [109], but no fluorescence of $N_2O^+(B)$ and $N_2O^+(C)$ states has been observed. At about 18 eV, $N_2O^+(B)$ state decays essentially by dissociation to $N_2^+(X^2\Sigma_g^+)$ and NO$^+$. The minimum energy required for the formation of $N_2^+(B^2\Sigma_u^+,v_0=0)$ from $N_2O$ is 20.4 eV, which is close to the dissociation limit.
Figure 4.16 Portion of fluorescence spectrum from Fig. 4.15. The fragment transition $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+) \nu^+ = 0 \rightarrow \nu'' = 0$ near the $N_2O^+(A^2\Sigma^+ \rightarrow X^2\Pi) \nu^+ = (0,0,0) \rightarrow \nu'' = (2,0,0)$ is shown. It is created from the photoionization of neutral ground state $N_2O$, $\nu_0 = (0,0,0)$; $h\nu_{exc} = 50 \text{ eV}$.

of $N_2O^+(C^2\Sigma^+)$ state. Bearman et al. [151] have proposed that the $N_2O^+(C^2\Sigma^+)$ state is the main source of the $N_2^+(B \rightarrow X)$ emission. Examination of the $N_2O^+$ correlation diagram of Lorquet and Cadet [150] suggests that these products correlate to a high-lying potential energy surface, and a crossing with the $N_2O^+(C^2\Sigma^+)$ state surface is possible. The formation of $N_2^+(B^2\Sigma_u^+)$ from $N_2O$ has been observed by photoionization [112], electron impact [152,153], 20-1000 eV $\text{He}^+$ and $\text{Ne}^+$ ions impact [151], and by Penning ionization [154].
Table 4.11. Lower threshold energy limits for dissociative ionization (DI) within $12 \leq h\nu_{\text{exc}} \leq 22$ eV \textsuperscript{a,b}.

<table>
<thead>
<tr>
<th>DI</th>
<th>Dissociation products</th>
<th>Dissociation threshold (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI1</td>
<td>$\text{NO}^+ (X\Sigma^+) + \text{N}(4\text{S})$</td>
<td>14.187</td>
</tr>
<tr>
<td>DI2</td>
<td>$\text{N}_2 (X^1\Sigma_g^+) + \text{O}^+$</td>
<td>15.289</td>
</tr>
<tr>
<td>DI3</td>
<td>$\text{NO}^+ (X^1\Sigma^+) + \text{N}(2\text{D}_0)$</td>
<td>16.571</td>
</tr>
<tr>
<td>DI4</td>
<td>$\text{N}_2^+ (X^2\Sigma_g^+) + \text{O}(3\text{P})$</td>
<td>17.251</td>
</tr>
<tr>
<td>DI5</td>
<td>$\text{NO}^+ (X^1\Sigma^+) + \text{N}(2\text{P})$</td>
<td>17.763</td>
</tr>
<tr>
<td>DI6</td>
<td>$\text{N}_2^+ (A^2\Pi_u) + \text{O} (3\text{P})$</td>
<td>18.364</td>
</tr>
<tr>
<td>DI7</td>
<td>$\text{N}_2 (X^1\Sigma_g^+) + \text{O}^+ (2\text{D})$</td>
<td>18.614</td>
</tr>
<tr>
<td>DI8</td>
<td>$\text{N}_2^+ (X^2\Sigma_g^+) + \text{O} (1\text{D})$</td>
<td>19.218</td>
</tr>
<tr>
<td>DI9</td>
<td>$\text{NO}(X^2\Pi) + \text{N}^+ (3\text{P}_0)$</td>
<td>19.472</td>
</tr>
<tr>
<td>DI10</td>
<td>$\text{N}_2^+ (A^2\Pi_u^+) + \text{O} (1\text{D})$</td>
<td>20.301</td>
</tr>
<tr>
<td>DI11</td>
<td>$\text{N}_2 (X^1\Sigma_g^+) + \text{O}^+ (2\text{P})$</td>
<td>20.306</td>
</tr>
<tr>
<td>DI12</td>
<td>$\text{N}_2^+ (B^2\Sigma_u^+) + \text{O}(3\text{P}_2)$</td>
<td>20.421</td>
</tr>
<tr>
<td>DI13</td>
<td>$\text{NO}^+ (A^3\Sigma^+) + \text{N}(4\text{S}_0)$</td>
<td>20.580\textsuperscript{c}</td>
</tr>
<tr>
<td>DI14</td>
<td>$\text{NO}(X^2\Pi) + \text{N}^+ (1\text{D})$</td>
<td>21.370\textsuperscript{c}</td>
</tr>
</tbody>
</table>

(a). These energies are calculated with dissociation energies of $\text{N}_2^-\text{O} (1.677 \text{ eV})$, $\text{N}-\text{NO} (4.930 \text{ eV})$ taken from ref. [36], together with the energy levels of $\text{N}_2$ and $\text{NO}$ molecules given by ref.[36], and the energy levels of the N and O atoms given by ref.[112]. (b). from reference [112]. (c). from reference [150].

Figure 4.17 presents the CIS spectrum of fragment $\text{N}_2^+ (B^2\Sigma_u^+)$ for the vibrational level $v^+ = 0$ in the incident photon energy range $20 \leq h\nu_{\text{exc}} \leq 150$ eV. Since the CIS spectrum shows prominent features in the 40-60 eV region, the
dissociative photoionization channels of interest are in the inner valence region. At that energy region, it has been well documented that several dissociative double ionization channels [84,148] open up. In other words, double as well as single ionization is possible.

4.2.1.3 Discussion

Identification of Resonance-Like Feature Observed in Cross Section Spectrum: The energy dependence of the CIS spectrum of $N_2^+(B^2\Sigma_u^+)$ (Fig. 4.17) shows two prominent dissociation onsets and a broad enhancement at $\sim 50$ eV: the first onset is at 20 eV; the cross section rises from second threshold ($\sim 40$ eV) to a broad maximum (40-60 eV) and falls off slowly towards higher energies. It is the broad resonance-like feature at 50 eV that I wish to characterize. In the earlier study by Hitchcock and co-workers [155], the total cross section curve of $N_2^+$ fragment from the ionization of $N_2O$ was generated: the ion fractions derived from the TOF spectra were combined with the photoabsorption spectra derived from the (e, 2e) study [156] and ionization efficiency [157] to obtain the photofragmentation oscillator strength of $N_2^+$. However, there is no resemblance between the current CIS curve and the result by Hitchcock et al. (see, fig. 6 in ref. [155]). No broad enhancement was observed in their spectrum. This is due to the fact that Hitchcock et al. were unable to detect any $N_2O^{++}$ ions in their electron impact investigation of fragmentation of $N_2O$. Furthermore, multiple electron transition (MET) effects above 24 eV were not taken into consideration in the dipole breakdown scheme (see ref. [155], fig.11).
Figure 4.17 Constant-ionic-state spectrum of fragment $N_2^+ (B^2\Sigma_u^+)$ state $v^+ = 0 \rightarrow v'' = 0$. First onset is labeled as DI12 at 20.421 eV (see Table 4.II); second onset is labeled as DDI (dissociative double ionization) at 40 eV.

The first onset at ~ 20 eV is interpreted as the lowest dissociative ionization limit for the production of $N_2^+ (B^2\Sigma_u^+)$ and other fragments based on Table 4.II. There is another distinct feature in the energy region $h\nu_{exc} \sim 40$ eV, which is consistent with the opening of another dissociation channel contributing to the formation of the $N_2^+ (B^2\Sigma_u^+)$ accompanied by a $O^+$ fragments, i.e., this second onset is the double positive ion pair formation $N_2O^{++} \rightarrow N_2^+ (B^2\Sigma_u^+) + O^+(4S_u)$, a process which requires a minimum energy of 39.7 eV [148]. This
interpretation is supported by the results of coincidence measurements [148,156]; the \( \text{N}_2^{++} \) \( \text{O}^+ \) channel is the most prominent process in total fluorescence detection following various dissociative double photoionization of \( \text{N}_2\text{O} \). These results give an indication of the highly unstable nature of parent ion \( \text{N}_2\text{O}^{++} \) in its ground state as well as excited states.

It is natural to suggest that the broad enhancement in the CIS curve represents the strongly repulsive nature of doubly ionized states of \( \text{N}_2\text{O} \) whose cores correspond to the correlation satellites in the binding energy region 35-50 eV. The CIS curve is almost linear over the region from 40 eV to 45 eV. Such a linear threshold behavior is expected in the case of double photoionization [140]. Therefore, the broad enhancement very likely tracks the total double ionization cross section curve. The integrated satellites cross section curve for \( \text{CS}_2 \), an isoelectronic triatomic molecule of \( \text{N}_2\text{O} \), has shown a striking similarity (bell shape) in its total double ionization cross section curve (see Fig.5 in ref. [143]). Unfortunately, the information required to determine whether the similarity holds for \( \text{N}_2\text{O}^{++} \) is not available. The energies of the doubly ionized states have not been calculated; furthermore, the total cross section curve for \( \text{N}_2\text{O}^{++} \) has not been established to test our prediction. On this basis, I conclude that the CIS spectrum of \( \text{N}_2^+(\text{B}^2\Sigma_u^+) \) might reflect its parent ionic state ionization cross sections.

The broad resonance-like feature is reminiscent of the shape resonance profile that is commonly observed in the ionization cross section for the \( \text{N}_2\text{O}^+ \) \( \chi^2\Pi, \text{A}^2\Sigma^+, \text{B}^2\Pi, \) and \( \text{C}^2\Sigma \) channels. This feature was interpreted as the \( 7\sigma \rightarrow k\pi \) shape resonant enhancement which showed up commonly through the coupling...
between partial continuum channels [51]. The single-particle excitation breakdown in the shape resonance requires the rearranging correlations to provide interchannel coupling to other particle channels. In N₂ and CO diatomic cases, interchannel coupling appears as a satellite band borrowing intensity from the near-degenerate single-hole 2σ⁻¹ and 3σ⁻¹ shape resonant continuum channels, respectively [147]. In analogy to these systems, we expect that in the excitation or decay process of the satellites within the inner-valence region for N₂O, the electron correlation with the 4σ⁻¹ (inner-valence hole) continuum might play an important role, i.e., multielectron configurations borrowing intensity via electron correlation from the single-hole 4σ molecular orbital. This hypothesis is based on several factors: first, the 4σ orbital intensity in N₂O is evidently spread over a considerable energy range [58,61,62,157] from 30 to 50 eV by the effect of final ionic states configuration interaction, though the contributions of 5σ, 6σ, and 1π ionization are not negligible in this energy region. Second, doubly ionized states have the nature of ionic satellites owing to their cores corresponding to the correlation satellites, and would show similarity in the intensity borrowing by configuration interaction. Third, the phenomena of shape resonance described for single channel should be widespread, as shape resonances appear to affect one or more inner- and outer-shell channels in most (nonhydride) molecules [4]. Finally, the contribution of σ→σ* resonance-like nature of 4σ→kσ transition will probably appear more clearly in the dissociative photoionization spectra, because such transitions to the σ antibonding orbitals are expected to loosen their participating bonds. An antibonding property of a shape resonance which induced non Franck-Condon behavior in vibrational population [40] may also drives the
outgoing nuclear motion toward the dissociation limit. Therefore, it is the shape resonance effects in final two-hole-one-particle ionization channels that leads interchannel coupling effects with single hole channel in the inner-valence dissociation dynamics.

As a conclusion remark, it should be noted that the broad enhancement in the present CIS curve was not observed in the photoabsorption spectrum [158] or photoionization yield spectrum [159]. This suggests that high-lying doubly ionized states as a result of final-state correlation become invisible due to their small oscillator strengths and a greater density of continuum ionization (single-continuum) in that energy region. In the dissociative photoionization process, however, the total contribution of the satellite structure is not negligible. For some inner valence orbitals, electron correlation effects are so large that single electron ejection occurs in a minority of events. It should also be stressed that the measurement of dispersed fluorescence emitted from ionic fragments can provide a sensitive tool in the almost totally unknown spectroscopy, in particular, the structure and relaxation of electronically excited states of doubly charged polyatomic cations.

Dissociation Mechanisms: The observation of emission only from the \( v^+ = 0 \) level indicates that most of \( \text{N}_2^+(B^2\Sigma_u^+) \) ions are populated in the ground vibrational level. In contrast, emissions from vibrational levels up to \( v^+ = 5 \) have been observed in the \( \text{He}^+, \text{Ne}^+ + \text{N}_2\text{O} \) reaction at an incident ion kinetic energy of 20-1000 eV [151]. The vibrational population distributions obtained under electron impact ionization are significantly different, two weak bands of \( \text{N}_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+) \) with \( v^+ = 0 \rightarrow v'' = 0 \) and \( v^+ = 0 \rightarrow v'' = 1 \) were
observed [153]. In Penning ionization [154], the dissociative charge-transfer process preferentially populates the excited vibrational levels ($v^+ = 0-4$) in the $N_2^+(B^2\Sigma_u^+)$ state. These results suggest that the energies of the projectile ions give an enhancement of the populations of the higher vibrational levels of the fragments. Obviously, there are different dissociation mechanisms involved in the photoionization process. This explains why there are no higher vibrational levels observed in previous [112] and current photoionization study.

Within $20 \leq h\nu_{exc} \leq 22$ eV, the possible precursor of $N_2^+(B^2\Sigma_u^+)$ is the $N_2O^+(C^2\Sigma)$ state which decays completely by predissociation into $N_2^+(B^2\Sigma_u^+) + O$ (unknown state) [151] based on Table 4.II. The PES of $N_2O^+(C^2\Sigma)$ state was observed with a relatively short progression; the Franck-Condon factor is largest for the $(0,0,0)$ band and the vibrational frequencies as nearly same as those in the ground $N_2O$ state [109]. These characters indicate that $N_2O^+(C^2\Sigma)$ results from the removal of a non-bonding electron, and the minimum positions and shapes of the potential surface are quite similar for the $N_2O^+(C^2\Sigma)$ state and the $N_2O (X^{1\Sigma_g^+})$ ground state. Therefore, the vertical ionization of $N_2O$ favorably produces the $N_2O^+[C^2\Sigma, \nu_0=(0,0,0)]$ state, hence, leads to ionic fragments $N_2^+(B^2\Sigma_u^+)$ in the ground vibrational level.

In inner-valence region, the lowest energy two-hole configuration of $N_2O^{++}$ appears to be primarily $3\Sigma^{-1}(2\Pi)^2$ (39.7eV) character [160]. The dominance of the $(2\Pi)^2$ configuration of low-lying $N_2O^{++}$ represents relative low ionization energy and can be reached either by direct path from $N_2O (X^{1\Sigma_g^+})$ or a sequential mechanism involving the stable electronic state $N_2O^+(X^2\Pi)$ state which has a $2\pi$ hole. Since the difference in the equilibrium internuclear
separation between the $N_2O(X^1\Sigma^+)$ and $N_2O^+(X^2\Pi)$ states is $\sim 0.02\text{Å}$ [108], it is assumed that molecular double ionization occurs at the internuclear separation close to the equilibrium value for the neutral $N_2O$. Namely, the transition occurs nearly vertically. It implies that during the course of dissociation the energy transfer process occurs quite rapidly. For part of the dissociation energy to be converted into the internal energy of ionic fragments, the dissociating products must separate sufficiently slowly for efficient energy exchange to occur. Obviously, this will not be favored in the case of strong repulsive Coulombic forces between the cationic products.

Most importantly, the present study confirms that the dissociation of doubly charged cations is highly exothermic [136, 160], i.e., most of the initial energy is converted into kinetic energies of the fragments rather than into the internal energy distributions of the ionic fragments. The earlier coincidence study of $N_2O^{++}$ [148] determined that the kinetic energy release for products $N_2^+ + O^+$ is 5.6 eV. This result is not surprising. It has been found that in the $SO_2^{++}$ case [145], the conversion of internal energy of the parent doubly charged cation into kinetic energy of the ionic fragments ($SO^+ + O^+$) is almost complete (90%); more than 80% of the initial energy is converted into kinetic energy of the products in the $CO_2^{++}$ dissociation [160]. All of these results indicate that a direct dissociation leads to the rapid energy transfer, thus, the vibrational selectivity in the doubly ionized ion dissociation processes.

Finally, studies of the dissociation pathways of $N_2O^{++}$ can reveal interesting information about the dynamics of double ionization. The possible
proceeds of the doubly-charged ion $N_2O^{++}$ can be described as in Eq.4.4(a),(b),(c):

\[
N_2O^{++} \rightarrow N_2O^{++} \quad (4.4a)
\]
\[
\rightarrow N_2^+ + O^+ \quad (4.4b)
\]
\[
\rightarrow N_2^{++} + O \quad (4.4c)
\]

The process (4.4a) simply means that $N_2O^{++}$ ions remain as the parent ions owing to their metastable nature in a (sub)microsecond time scale, which have been observed in mass spectrometry [156]. The process (4.4b) occurs under the conditions that two holes in $N_2O^{++}$ are on the different sites during the course of separation of the $N_2^+$ and $O^+$ ions, which means two ejected electrons are of bonding nature, removal of these two electrons weakens the bonding. The process (4.4c) is attributed to the localization of the two holes in the $N_2O^{++}$, i.e., two holes are on the same site at least during the course of the dissociation. However, no such $N_2^{++}$ has been observed for $N_2O$. The reason is that the thermochemical threshold for the process (4.4b) is generally lower than that for the (4.4c). If the double ionization occurs from the outer valence orbitals, the process (4.4b) is favored as compared with the process (4.4c) because of Coulombic repulsion between two positive charges on different sites. In contrast, in the region where at least one electron is ejected from inner valence orbitals, the process (4.4c) does occur because of somewhat localized nature of electrons. Site-specific characters of double ionizations in the inner-valence regions would be due to a main contribution of 2s electron in N and O atoms to the two-hole final states.
4.2.1.4 Conclusion

An excitation yield curve for the N$_2^+$ fragment was generated from the fluorescence spectra to observe peaks corresponding to various dissociative ionization channels. I have been successful in ascertaining information on the internal energies of the fragments via their dispersed emissions and in identifying the energy regions in which the dissociative single, double ionization processes occur, and multielectron transitions contribute. The aspects of dissociative double photoionization in the inner-valence region were discussed; the broad enhancement in 40-60 eV is tentatively attributed to the strongly dissociative nature of doubly ionized states of N$_2$O correlating with ionic satellites and the single-hole continuum channel 4σ. The breakdown of single-particle excitation model has shown important consequence for the understanding of dissociative photoionization.

The results demonstrated that detailed vibrationally resolved dispersed fluorescence measurements of individual fragments can provide a sensitive tool to reveal dissociation channels and internal energy distributions for the respective ions which are not apparent in other studies. Dispersed fluorescence study has its place together with various coincidence techniques and PES. Useful information can be gleaned from each method, and they are interesting in their own right.

Finally, it should be emphasized that it is difficult to analyze the shape of partial cross section curve for ionic fragments in the absence of calculations of total double ionization cross section curves. We are unfortunately beyond present theoretical progresses. Therefore, the experimental results are reported together
with limited discussions here in order to stimulate theoretical investigations of this interesting case.
Chapter 5

Conclusions

I have used measurements of dispersed fluorescence from electronically excited photoions to probe molecular aspects of photoionization dynamics, i.e., vibration and dissociation. Vibrational branching ratios are generated and their non-Franck-Condon behavior is used as a probe to investigate shape resonances and their induced effects, such as interchannel coupling. In particular, vibrationally resolved data provide a means of investigating the correlation of electronic and nuclear degrees of freedom over an extremely broad range (3 ≤ E_k ≤ 200 eV). It is found that molecular photoionization retains its molecular character over a range which is usually assumed to be dominated by atomic-like behavior.

The results of these studies demonstrate the power of dispersed fluorescence measurements to resolve very low frequency molecular motion (i.e., vibration). The advantage of using this strategy is that the detection bandwidth is decoupled from the excitation bandwidth, in contrast to photoelectron measurements where the excitation bandwidth is the lower limit to the overall resolution. In addition to resolving the energy of the fluorescence transitions, it can reveal information on internal energy distributions of ionic fragments from dissociative ionization and dissociation channels as well. Furthermore, the intense tunable synchrotron radiation coupled to the high resolution of this technique
provides us opportunities to access weak ionization channels, such as excited bending, which may be strongly affected by resonant processes. The current results stress the importance of this capability in uncovering new trends in resonant molecular photoionization dynamics.

The role of molecular geometry in polyatomic shape resonant photoionization is further characterized by probing an alternative vibrational mode, i.e., the ramifications of shape resonances on bending vibrations are studied in detail for the first time over a broad energy range (20 \( \leq \hbar \nu_{exc} \leq 100 \) eV). Bending excitation is created from vibrationally hot target molecule (hot band excitation), and this probe of vibrational distributions shows non-Franck-Condon behavior. The comparison of two isoelectronic molecules \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) reveals different behavior. The bending mode of the \( \text{N}_2\text{O}^+ (A^2\Sigma^+) \) state shows much more dramatic deviation from the ground vibrational level than does that of the \( \text{CO}_2^+ (B^2\Sigma_u^+) \) state. The results are interesting and suggest the hypotheses that shape resonances may be sensitive to molecular symmetry, i.e., reducing the symmetry by bending causes different coupling of alternative symmetry continuum channels. A simple physical picture in terms of a linear triatomic molecule serves well in accounting for the change of the potential barrier: bending motion may change the width of the “box” where the photoelectron is trapped. They also underscore the need for calculations to interpret the shape resonance effects on bending motion. Using the vibrational motion as a probe of internuclear distance provides qualitative information on the nature of the trapping site of the resonant state in a polyatomic molecule.
While previous $7\sigma^{-1}$ photoionization studies of N$_2$O are limited to the $hv_{exc} \leq 55$ eV ($E_k \leq 35$ eV), my work extends the range by an order of magnitude; the vibrationally resolved data have been obtained at kinetic energies exceeding 230 eV. The results are illuminating, wide-ranging Franck-Condon breakdown is observed in both symmetric and asymmetric stretching modes. The origin of this non-FC behavior is tentatively attributed to two likely mechanisms and both may play a role. The low energy FC breakdown results from the strong shape resonance at 20 eV; high energy non-FC behavior may be related to Cooper minima. It is the first such result ever obtained for a polyatomic molecule, and surely it provides challenge and an interesting case for theoretical study.

CO$_2$ $3\sigma_u^{-1}$ photoionization (which is valence isoelectronic with N$_2$O $7\sigma^{-1}$ photoionization) is also investigated, and our data are the first (and only) vibrationally resolved results for this channel. Two resonance features are observed: a low energy resonance attributed to autoionization and a high energy enhancement is consistent with the previous calculated continuum channel coupling mediated shape resonance between $(4\sigma_g)^{-1}$ and $(3\sigma_u)^{-1}$ channels for photoionization of CO$_2$. The agreement between experiment and calculation is satisfactory. These results provide a good test for theoretical methods aimed at understanding interchannel coupling. The present vibrationally resolved studies for $7\sigma^{-1}$ N$_2$O and $3\sigma_g^{-1}$ CO$_2$ shape resonant photoionization demonstrate that vibrationally resolved data can highlight microscopic aspects of the scattering dynamics since different internuclear configurations can be probed by sampling
alternative vibrational modes (symmetric stretch, asymmetric stretch and bending mode).

Complementary to coincidence measurements between the fragment ions, we have been successful in measuring dispersed fluorescence from an individual ionic fragment for the first time over a broad spectral range to elucidate the underlying dynamics of dissociative photoionization. Rich information is revealed on dissociation channels and internal energy distributions for the respective fragments which are not apparent in coincidence measurements. In this dissociative photoionization study of N$_2$O, I identified the energy regions in which the dissociative single and double ionization processes occur, and multi-electron transitions contribute. The dissociative double ionization which occurs following the excitation or ejection of inner-valence electrons is a region which is strongly influenced by correlation effects, and may be correlated with ionic satellites and the single-hole shape resonance continuum channel. In other words, these results suggest that the yield of the ionic fragments may reflect the nature of parent ionic states. These results also underscore the fact that intensity borrowing occurs in the outer-valence region as well as inner-valence region. Most importantly, the dissociative single and double photoionization study opens a new avenue for probing correlations between electronic and nuclear degrees of freedom. Determination of the final state distributions of fragments probes the electronic and nuclear motion of the collision complex responsible for the asymptotic fragment distributions.

For all these experimental successes, theoretical calculations are still needed for providing additional quantitative and qualitative insights. Frozen-core Hartree-
Fock calculations for \( N_2O \) (7\( \sigma^- \)) are available in the lower energy region, but are not available for a broad enough energy region or for geometries representative of the bending vibration. Cooper minima-induced Franck-Condon breakdown has been calculated for \( N_2 \) [114], and future work on \( N_2O \) may help us clarify the nature of Cooper minima in polyatomic systems.

Finally, the unifying theme shown of this dissertation is the correlation between electronic and nuclear degrees of freedom in molecular photoionization dynamics. Attempts have been made to investigate such correlations via dispersed fluorescence measurements in polyatomic molecules. Molecular aspects of the photoionization dynamics can be extracted with great precision even at very high photoelectron energies.
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Vita

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