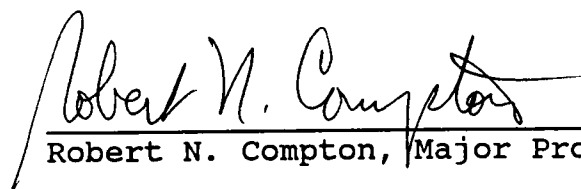


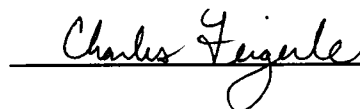
To the Graduate Council:

I am submitting herewith a dissertation written by Stanley Jacob Bajic entitled "Multiphoton Ionization Photoelectron Spectroscopy of Rare Gases and Multiphoton Excitation of Alkalies." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


Robert N. Compton, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:


Vice Provost
and Dean of The Graduate School

Multiphoton Ionization Photoelectron Spectroscopy
of Rare Gases
and
Multiphoton Excitation of Alkalies

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Stanley Jacob Bajic

May 1991

To my parents

Acknowledgements

I would like to gratefully acknowledge Robert N. Compton who served as my advisor. His patience, understanding, knowledge, and enthusiasm has made this a most pleasurable endeavor. His resourcefulness and "knack" for science has been of tremendous aid in the direction of this work.

I would also like to thank Howard Carman and John Miller for their support and their tolerance of my constant pestering. Their assistance during the course of this work has been enormous.

In addition, I would like to acknowledge and thank the U. S. Department of Energy (Contract No. AC05-84OR21400 with Martin Marietta Energy Systems, Inc.) for their financial support.

Finally, I would like to warmly acknowledge Rikki Waterhouse for her friendship and constant support.

Abstract

Collisional relaxation of the $6s[3/2]_1$, $6s'[1/2]_1$, $5d[3/2]_1$, and the $7s[3/2]_1$ m_j levels of xenon has been investigated experimentally. Disalignment and dephasing of the m_j levels have been studied by measuring the pressure dependence of the ratio of the ionization from selectively excited $m_j=0$ and $m_j\pm 1$ sublevels in a three photon resonant ionization experiment employing novel use of two counterpropagating beams with parallel and perpendicular polarizations, respectively.

Angular distributions for energy resolved photoemitted electrons from resonantly enhanced multiphoton ionization (REMPI) via the two-photon allowed, $(2+1)$, $6p[1/2]_0$, $6p[3/2]_2$, $6p'[1/2]_0$, $6p'[3/2]_2$, $7p[1/2]_0$, $7p[3/2]_2$, and $7p[5/2]_2$ states, and the three-photon allowed, $(3+1)$, $7s[3/2]_1$, $8s[3/2]_1$, $9s[3/2]_1$, $5d[3/2]_1$, $5d'[5/2]_3$, and $5d'[3/2]_1$ states of xenon and the three-photon allowed, $(3+2)$, $5s[3/2]_1$, and the $(3+1)$ $6s[3/2]_1$, $4d[3/2]_1$, $4d[5/2]_3$, and $4d[7/2]_3$ states of krypton are reported. The measured angular distributions are compared to theoretically generated curves based on multichannel quantum defect theory (MQDT). Photoelectron energy and angular distributions for the REMPI process via the four-photon allowed, $(4+1)$, $6p[1/2]_0$ and $6p[3/2]_2$ states of xenon are also reported. Photoelectrons due to above threshold ionization, $(4+2)$,

resonantly enhanced via the four-photon allowed $6p[1/2]_0$ state are also observed.

Photoelectron energy distributions are also reported for resonantly enhanced multiphoton ionization via a number of two- and three-photon allowed transitions in ethylene and trans-1,3-butadiene. In addition, a detailed description of a double reflectron mass spectrometer is also given. Energy resolved angular distributions are reported for resonantly enhanced multiphoton ionization via the two-photon allowed $C^2\Pi$ state of ArNO.

Multiphoton excitation and ionization processes in dense (1-10 Torr) lithium, potassium, and sodium vapor was also studied. A number of different nonlinear processes were observed and reported including self focussing, stimulated electronic Raman scattering (SERS), stimulated hyper-Raman scattering (SHRS), and various four and six wave-mixing processes. Some of the more interesting processes studied involved hybrid resonances, conical emission, and third harmonic generation in sodium vapor.

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Chapter I

Introduction

Historical

Although two-photon absorption and emission processes were first addressed theoretically by Göppert-Mayer^{1,2} as early as 1929, the first experimental observations of multiphoton processes were not made until the early 1950's in the radio frequency region of the spectrum. Hughes and Graber³ observed a unpredicted line group at one-half the frequency of one of the line groups in the spectrum of Rb^{85}F using the electronic resonance method. Later Brossel et al.,⁴ reported higher-order resonances requiring "several quanta" in a magnetic resonance experiment of oriented sodium atoms.

Studies of multiphoton processes in the visible region of the spectrum began with the invention of the laser. In 1961, Franken et al.,⁵ focussed a ruby laser (6942 Å) into a quartz crystal and observed the generation of second harmonic ultraviolet radiation (3471 Å). Almost simultaneously, Kaiser and Garret⁶ observed strong two-photon absorption from a ruby laser in $\text{CaF}_2:\text{Eu}^{2+}$ crystals by monitoring the fluorescence of the Eu^{2+} ion. Abella,⁷ also using a ruby laser, studied the two-photon absorption of the

$6s\ ^2S_{1/2} \rightarrow 9d\ ^2D_{3/2}$ transition in cesium by monitoring the fluorescence decay from the $9d\ ^2D_{3/2}$ state to the $6p\ ^2P_{3/2}$ state.

The first two-photon absorption study on a crystal was done by Peticolas et al.,⁸ in 1963. Using only one ruby laser, they obtained the two-photon absorption cross section for crystalline anthracene at 6942 Å. Later, Bergman and Jortner⁹ coupled a dye laser with a ruby laser and measured the two-photon absorption cross section for crystalline anthracene over a wider energy range. The long pulse length of the ruby laser required a point by point measurement at different pump frequencies resulting in a crude excitation spectrum. In 1973, Hochstrasser et al.,¹⁰ published the first high resolution, vibrationally resolved, two-photon absorption spectrum of an organic crystal. Using a N_2 pumped dye laser, they continuously recorded the absorption spectrum, from 6100 Å to 5700 Å, of the biphenyl crystal at 2° K.

In 1972, Lineberger and Patterson¹¹ observed resonant two-photon photodetachment of electrons from C_2^- . The experiment involved crossing a beam of C_2^- ions with a tunable dye laser. By tuning the dye laser, the authors were able to record the two-photon photodetachment cross section of C_2^- demonstrating that multiphoton spectroscopy can be used to investigate the electronic structure of molecular negative ions.

Two-photon absorption of molecules in the gas-phase was first observed in benzene by Hochstrasser et al.¹² This experiment demonstrated the advantage of gas-phase studies where frequency shifts due to the medium are eliminated. The first assignment of new molecular states based on hot-band analysis after two-photon excitation of the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition in benzene was made by Wunch et al.¹³ The two-photon absorption was monitored by the fluorescence emitted from the upper excited state. Their assignments were later confirmed by polarization studies of Bray et al.¹⁴ Other two-photon studies were performed in order to observe and characterize new states in molecules, including naphthalene,¹⁵ nitric oxide,¹⁴ and iodine¹⁶ soon followed.

Vasilenko et al.¹⁷ proposed in 1970 that the simultaneous absorption of two counter-propagating photons by an atom can eliminate inhomogeneous Doppler broadening of spectral lines. This is known as "Doppler-free" two-photon spectroscopy. Upon absorption of a photon, an atom in the gas phase possessing any velocity component in the direction of the propagation of light will experience a shift in its resonant frequency $\omega = \omega_1 + \vec{k} \cdot \vec{v}$, where $\vec{k}$ is the direction wavevector and $\vec{v}$ is the relative velocity of the atom. When the same atom absorbs a second photon of equal energy travelling in the opposite direction $\omega = \omega_2 - \vec{k} \cdot \vec{v}$, it will also experience a shift of equal magnitude but opposite in direction. The two shifts will cancel each other out

producing a homogeneous linewidth of the resonance transition. Experimental observation of the first two-photon Doppler-free spectra was reported by several workers who examined the hyperfine splittings of several excited states of sodium.^{18,19}

Bunkin and Prokhorov²⁰ predicted that if the laser intensity is sufficiently high, multiphoton ionization will dominate over other multiphoton processes. Keldish²¹ was the first to provide a rigorous theoretical treatment of multiphoton ionization. The first experimental observation of a multiphoton ionization process was reported by Voronov and Delone²² in xenon which required the absorption of seven photons from a Q-switched ruby laser. Popescu et al.²³ utilized the sensitivity of this technique and investigated the two-photon allowed $ns\ ^2S$ and $nd\ ^2D$ intermediate states in cesium. A number of articles reviewing the general area of multiphoton ionization spectroscopy have been published.²⁴⁻²⁷

Other applications of multiphoton spectroscopy have involved frequency doubling of high powered visible lasers to conduct high resolution studies of high lying excited states of CO and N₂ by two-photon absorption spectroscopy.²⁸ These high lying excited states were observed by monitoring the vacuum ultraviolet fluorescence emitted from these states.

An additional aspect of multiphoton spectroscopy has

involved the study of frequency conversion to regions outside the visible spectrum. Generation of third harmonic vacuum ultraviolet light from the absorption of three-photons of the same frequency was first reported by Ward and New.²⁹ Further studies have investigated the absorption of three-photons of different frequencies to produce tunable ultraviolet and infrared radiation with reasonably high conversion efficiencies³⁰⁻³² in sum and difference frequency generation.

In this thesis, multiphoton spectroscopy was used in the investigation of rare gases and alkali metals. Chapter II examines the influence of collisional m_j -mixing on resonantly enhanced multiphoton ionization in xenon. Chapter III employs photoelectron spectroscopy to further investigate the dynamics of resonantly enhanced multiphoton ionization of rare gases and various molecules. Chapter IV presents some new observations of multiphoton processes in dense alkali vapors upon two- and three-photon resonant excitation. The rest of this chapter presents some general theory of multiphoton processes.

Theory

The purpose of this section is to provide a theoretical basis of multiphoton processes. For a more detailed

discussion and analysis the reader is referred to the following reviews^{24,26} and references therein. For illustrative purposes a two-photon transition between two discrete levels can be thought of as two consecutive single photon transitions such that the sum of their energies is equal to the energy separation between an initial and final state. The first transition involves the absorption of one photon from the ground state, $|g\rangle$, leading to a virtual level, $|k\rangle$. Absorption of a second photon from the virtual level leads to a final state, $|f\rangle$.

By applying second order perturbation theory, the two-photon absorption cross-section can be written as²⁶

$$\sigma^2 = 8\pi^3 \left(\frac{e}{\hbar c} \right)^2 (\hbar\omega)^2 \left| \sum_k \left\{ \frac{\langle f | \vec{r} \cdot \vec{e} | k \rangle \langle k | \vec{r} \cdot \vec{e} | g \rangle}{\hbar(\omega_{gk} - \omega_1)} + \frac{\langle f | \vec{r} \cdot \vec{e} | k \rangle \langle k | \vec{r} \cdot \vec{e} | g \rangle}{\hbar(\omega_{gk} - \omega_2)} \right\} \right|^2 (I-1)$$

Since each matrix element must be nonvanishing, i. e. single photon selection rules, the selection rules for two-photon transitions will allow transitions between states of the same parity. In atomic spectroscopy, $s \rightarrow s$ and $s \rightarrow d$ transitions are allowed in two-photons. In addition, molecular two-photon selection rules for rotational transitions will be of the form $\Delta J=0, \pm 1$, or ± 2 and for homonuclear diatomics $u \rightarrow u$ and $g \rightarrow g$. A summary of two-photon selection rules for all possible polarization combinations can be found in a review article by Bonin and McIlrath.³³ Three-photon selection rules can be found in the general discussions presented by Grynberg³⁴ and McClain.³⁵

Obviously, one of the great advantages of multiphoton spectroscopy is the ability to reach and study excited states which are not accessible by single photon transitions from the ground state.

In general, the transition probability of a multiphoton ionization processes can be written as²⁶

$$W^{(N)} = \sigma^{(N)} I^N, \quad (\text{I-2})$$

where I is the laser intensity and $\sigma^{(N)}$ is the generalized cross-section of a N -photon process in units of $\text{cm}^{2N} \text{sec}^{N-1}$. The generalized cross-section may be written as

$$\sigma^{(N)} = \frac{(2\pi\alpha)^N}{4\pi^2} \frac{mK}{\hbar} \omega^N \int |M_{fg}^{(N)}(\Omega_k)|^2 d\Omega_k, \quad (\text{I-3})$$

where α is the fine structure constant, $\hbar$ is the Planck constant, m is the electron mass, Ω_k is the solid angle of the photon beam, and K is the wavevector of the outgoing electron. The matrix element, $M_{fg}^{(N)}$ is given by

$$M_{fg}^{(N)} = \sum_{k_{N-1}} \sum_{k_2} \sum_{k_1} \frac{\langle f | \vec{r} \cdot \vec{e} | k_{N-1} \rangle \dots \langle k_2 | \vec{r} \cdot \vec{e} | k_1 \rangle \langle k_1 | \vec{r} \cdot \vec{e} | g \rangle}{(\omega_{k_{N-1}} - (N-1)\omega) \dots (\omega_{k_2} - \omega) (\omega_{k_1} - \omega)}. \quad (\text{I-4})$$

Transition matrix elements are obtained from direct calculation, e. g. from quantum defect theory.³⁶ Except for hydrogen or hydrogen-like ions,^{37,38} calculation of $M_{fg}^{(N)}$ is usually rather difficult due to evaluation of infinite sums over intermediate states and the continuum which usually slowly converge.³⁹

When the incident exciting frequency is degenerate with

resonances in the medium, terms in the denominator of equation I-4 approach zero, the magnitude of equation I-3 increases, and an enhancement is observed in the ionization signal. This is known as resonantly enhanced multiphoton ionization. In order to keep the resonant enhancement finite an imaginary term is introduced into the denominator. For a thorough discussion of resonantly enhanced multiphoton ionization the reader is referred to the review articles by Lambropoulos.^{24,26}

AC Stark Effect

A phenomenon usually associated with high laser fields is known as the ac Stark effect. This effect results in a shift of the multiphoton resonance. The extent of the ac Stark effect is dependent of the power density of the exciting source and the Rabi frequency between the coupled levels in multiphoton process. The ac Stark effect is described as a virtual transition of nonresonant light between shifted atomic or molecular energy levels brought about by the field of the exciting source in an optical process. These shifts are not restricted to high power pulsed laser studies for they have been observed in low power, cw dye laser experiments.⁴⁰

Since the ac Stark effect was observed in a number of

studies presented in this manuscript, a small discussion is presented, describing this effect. The shift of a level, f , in a field E , is given by perturbation theory as ⁴¹

$$\Delta E_f = \frac{1}{4} E^2 \sum_g \left[\frac{|V_{fg}|^2}{(E_f - E_g - \hbar\omega)} + \frac{|V_{fg}|^2}{(E_f - E_g + \hbar\omega)} \right] \quad (\text{I-5})$$

where V_{fg} is the transition dipole matrix element between states f and g . The upper and lower levels experience equal but opposite shifts. When the applied frequency is $\nu < \nu_0$ the perturbation causes the distance between the levels to increase and when the applied frequency $\nu > \nu_0$ the perturbation causes the distance between them to decrease.

In a strong field, the levels are actually split into two sublevels with their positions given by⁴²

$$E_f^{1,2} = E_f + \frac{\delta}{2} \pm \left[\left(\frac{\delta}{2} \right)^2 + V_{12}^2 \right]^{1/2} \quad (\text{I-6})$$

and

$$E_g^{1,2} = E_g - \frac{\delta}{2} \pm \left[\left(\frac{\delta}{2} \right)^2 + V_{12}^2 \right]^{1/2} \quad (\text{I-7})$$

where $\delta = \Omega_{fg} - k\nu$ and represents the detuning of the applied frequency from the resonance transition. Here, Ω_{fg} is the Rabi frequency between levels f and g . For the simple case of a two-level system equation I-5 reduces to⁴²

$$\delta\nu = \frac{1}{4} E^2 \frac{|V_{fg}|^2}{\hbar(\nu_0 - \nu)} \quad , \quad (\text{I-8})$$

where $h\nu_0 = E_f - E_g$ and $\nu = \omega/2\pi$, is the applied frequency.

The ac Stark effect shows up as broadened asymmetric signals in a multiphoton ionization experiment. Physically, it can easily be understood how the ac Stark effect is manifested in a multiphoton ionization experiment employing focussed, pulsed lasers. When the frequency of the laser is tuned to be degenerate with a resonance in an atom, it will also be nearly degenerate with one of the resulting split levels. This results in virtual transitions between the split levels in the excited and ground state and appears as a energy shift in the spectrum. Pulse lasers that are employed in multiphoton ionization experiments have associated with them large spatial and temporal intensity fluctuations. Hence, a range of shifts will be experienced by the atom during the laser pulse and appears as a broadened and usually shifted asymmetric signal in the multiphoton ionization spectrum.

The ac Stark effect was described by Autler and Townes⁴³ in an experiment where a strong rf-field was used to produce transitions between two energy levels in OSC gas molecules. A second, weaker microwave field was then scanned and an absorption spectrum obtained which showed the splitting of the energy levels.

Chapter II

Collisional M_j -Mixing in Xenon

Introduction

The excitation of atoms or molecules by linearly (circularly) polarized light can allow for the preparation of an aligned (oriented) excited state. Alignment and orientation refers to the population distribution of the magnetic m_j sublevels as shown in figure II-1. The anisotropy in the distribution of m_j levels arises from selection rules in the multiphoton excitation process. For example, if we examine a two-photon transition, using a linearly polarized laser beam, in a rare gas atom in the np^6 1S_0 , $J=0$, ground state, selection rules allow excitation to a $n'p$ 1D , $J=2$ state. Furthermore, selection rules only allow $\Delta m_j=0$. Hence, for $J=2$, only the $m_j=0$ level is populated out of the five degenerate magnetic sublevels. Since the magnetic sublevels are non-statistically populated the atom is said to be aligned with respect to the laser field. An interesting facet of anisotropy which occurs during a multiphoton ionization process is the destruction of the alignment during a collision process. If multiphoton ionization experiments are conducted at sufficient pressures at which collisions can occur between the laser prepared

$J=2$

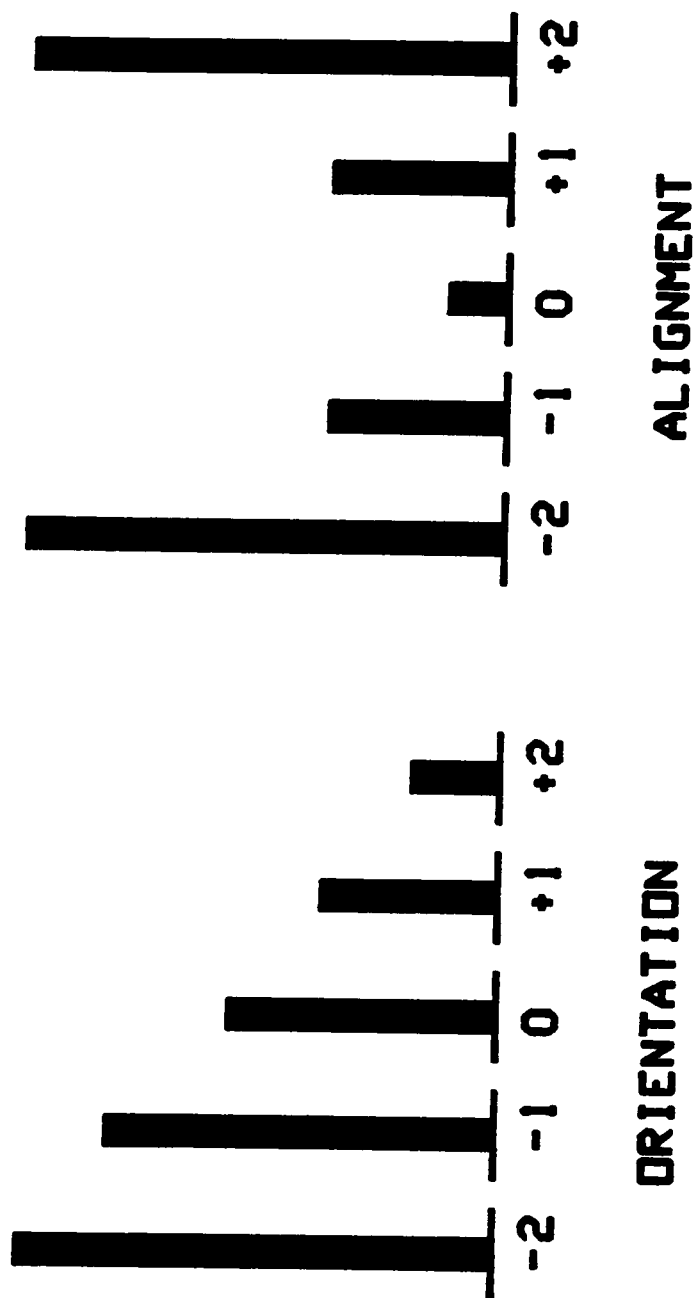


Figure II-1. Schematic representation of population distribution of magnetic sublevels for $J=2$ angular momentum.

excited state and a buffer gas, collisional depopulation of the $m_j=0$ level can be observed. Along with collisional depopulation of the m_j levels, a variety of other processes can occur when an excited-state atom collides with a buffer gas atom. Excluding Penning ionization or charge transfer, some of the other processes can involve relaxation of the excited state coherence⁴⁴ (also known as dephasing), transfer of coherence⁴⁵ and polarization⁴⁶ to another atom, or energy transfer between fine structure levels within an atom⁴⁷ or between different atoms.⁴⁸

Coherences arise from the optical pumping process. Initially, a coherent superposition of excited states are populated. Quantum mechanically, these states can be represented as a linear superposition of energy eigenstates which are related with a certain phase. In the density matrix formalism, if these phases are correlated or in-phase then a "coherence" exists, represented by the non-vanishing off-diagonal elements in the density matrix. If a collision or any other type of perturbation occurs which causes the relative phases to proceed at different rates, a disruption or a "dephasing" of the coherence occurs.⁴⁹

Investigations concerning collisional repopulation in atoms are also of intrinsic interest because collisional interaction mechanisms are usually not known in detail but are important in understanding and predicting processes involving energy transfer through gases. For example, an

important application involves investigating radiative and non-radiative energy transfer between atoms because of its importance in understanding energy pathways in the development of excimer lasers. Also, knowledge of collisional parameters is useful in determining properties of high temperature plasmas and for investigating interstellar matter.

The first studies of atomic collisions were conducted in pure alkali vapors⁵⁰⁻⁵³ and with various buffer gases^{54,55}. Traditionally, excitation of the alkali atom was performed with resonant radiation lamps or by electron bombardment and the effect of collisions followed by monitoring the change in the line shape or the depolarization of the fluorescence emission as a function of pressure. It became evident that such studies can provide a wealth of information on atom-atom interactions as well as collisional repopulation. Simple collision theories were employed to describe the observed lineshapes and used to calculate lifetimes of the excited states and various collision cross-sections.⁵⁶

Monitoring the fluorescence emitted from the excited atom became one of the most widely used methods to investigate collisional dynamics because of its simplicity. However, the results were subject to misinterpretation due to some inherent problems associated with the method. Some of these problems involved Doppler broadened excitation sources, "radiation trapping", and interference from

background emissions from the buffer gas.

Other methods were developed to circumvent the above mentioned problems. In 1924, Hanle⁵⁷ discovered that the fluorescence emission from an atom in a uniform magnetic field became depolarized as the direction of the magnetic field was reversed. It was shown that the depolarization was proportional to the lifetime of the excited state. This became known as the Hanle effect. Nearly twenty-five years later Colegrove et al.⁵⁸ discovered that at higher magnetic fields similar depolarization of the fluorescence signal occurred. Depolarization resulted from the fine or hyperfine levels crossing at some particular field. From these level crossing experiments lifetimes and Landé g-factors could be determined for the excited state. Brossel and Bitter⁵⁹ developed the "double resonance" method in which two resonant radiation sources were used together to examine depolarization of the fluorescence signal. A resonant radiation lamp was used to excite the atom and the depolarization of the fluorescence emission monitored as a function of an rf-field that was applied to induce transitions between the sublevels of the excited state.

These methods, fluorescence monitoring, Hanle effect, level-crossing spectroscopy, and double resonance spectroscopy provided the means from which numerous studies embarked to extract collision data from atoms and small molecules. The literature is too extensive to be recounted

here so the reader is referred to various reviews and the references therein.⁶⁰⁻⁶³

The development of the laser opened up a new vista for collision studies. Besides simply replacing conventional excitation sources, it allowed new variations on old methods (e. g. stimulated level-crossing^{64,65} and laser induced fluorescence⁶⁶⁻⁶⁹). Intensity and tunability of the laser allowed for depolarization studies to be conducted on a wide variety of molecules in different states of excitation since, in the past, one had to rely on fortuitous coincidences between molecular transitions and atomic lines from resonant radiation lamps. Collisional data was ascertained on metastable states that were formed by an electric discharge⁷⁰ and on excited states that are not optically connected to the ground state by using two-photon absorption techniques.^{71,72} The narrow bandwidth of the laser and Doppler-free techniques, such as optical-optical double resonance (OODR),⁷³ provided better resolution and selectivity of the magnetic sublevels. Silvers et al.,⁷⁴ first demonstrated the potential of OODR in collision studies by examining depolarization of state selected BaO (J, m_j) as a result of elastic ($\Delta J=0$) and inelastic ($\Delta J \neq 0$) collisions with CO₂. In the study of elastic collisions, one laser was used to prepare (pump) the BaO in the single $J=1, m_j=0$ sublevel of the first vibrational level of the A $^1\Sigma^+$ excited state. A second laser probed the extent of

collisional depolarization by inducing transitions to the $J=0$, $m_j=0$ level of the $C\ ^1\Sigma^+$ excited state from which the fluorescence was monitored. The polarization of the second laser was varied with respect to the first laser to further induce selected transitions between m_j levels. When the polarizations of the pump and probe lasers were parallel to each other, only $\Delta m_j=0$ transitions were allowed and the subsequent fluorescence from the $C\ ^1\Sigma^+$ excited state was due to initial $m_j=0$ population. When the polarizations were perpendicular, only $\Delta m_j=\pm 1$ transitions were allowed and any fluorescence from the $C\ ^1\Sigma^+$ excited state would be the result of collisionally populated $m_j=\pm 1$ levels of the $A\ ^1\Sigma^+$ excited state. Cross-sections were reported for m_j level mixing in BaO.

Snow et al.⁷⁵ used a variation of the OODR technique to study depolarization collisions of state selected NO $A\ ^1\Sigma^+$ (j, m_j) with various gases. Again, the first laser was used to align the molecule while the second laser used a bound-bound transition to probe the collisional depolarization. The polarization of the second laser was rotated and the intensity of the ionization signal monitored to examine the extent of depolarization as a function of gas pressure. In another experiment, state to state collision kinetics in NH_3 was investigated by Seelemann et al.,⁷⁶ by using an infrared laser to prepare selected $X\ NH_3$ JK levels of the ν_3 and ν_4 combination vibrations and an ultraviolet laser to conduct

resonantly enhanced (2+1) multiphoton ionization of the prepared states. State to state rate constants as well as identification of new vibrational levels of the B Rydberg state were reported. Using a resonantly enhanced two-photon ionization technique, Sasso et al.⁷⁷ reported m_j changing cross-sections for the $7p\ ^2P_{3/2}$ state of cesium for collisions with argon and helium. Other double resonance techniques, using microwaves and infrared light to study collisional depolarization, have also been reported.⁷⁸⁻⁸¹

More recently, Kedzierski et al.⁸² reported cross sections for m_j mixing and multipole relaxation of $6p\ ^2P$ Rb atoms for collisions with He, Ne, and Ar in a magnetic field.

Many other types of techniques employing lasers to study collisional depolarization include Hanle effects,⁸³⁻⁸⁶ laser induced line narrowing,⁸⁷ and molecular beam experiments.⁸⁸ The contributions to collisional studies using these and other laser based techniques have been enormous. The reader is referred to the reviews of Happer,⁶² Massey et al.,⁶³ Berman,⁸⁹ and Hertel and Stoll⁹⁰ for details of these contributions.

In this work, an experimental technique is introduced, utilizing resonantly enhanced multiphoton ionization to examine collisional interactions with an excited state and a buffer gas. This technique provides atomic parameters and collisional cross sections based on a theoretical

description of the experimental results using a system of rate equations derived from a full set of density-matrix equations.

The experiment involves the investigation of the collisional disalignment and dephasing of the resonantly excited $6s[3/2]_1$, $6s'[1/2]_1$, $7s[3/2]_1$ and $5d[3/2]_1$ states of xenon. The $j-1$ coupling notation is used to describe these excited states. The term in brackets represents the coupling of the spin plus orbital angular momentum of the core ($1/2$ or $3/2$) plus the orbital angular momentum of the outer electron. This term coupled with the spin of the outer electron yields the total angular momentum J , represented by the subscript.

The extent of disalignment and dephasing is measured by monitoring the ionization signal as a function of the gas pressure and angle of polarization of two laser beams in a counterpropagating arrangement. When polarized light is used to populate these levels, selective excitation of the magnetic sublevels is achieved. For $J=1$ there are three degenerate magnetic sublevels, $m_j=0, \pm 1$.

Experiment

The experimental setup for the collisional m_j -mixing experiment is shown in figure II-2. The output from a pulsed dye laser (Quanta Ray-PDL-1) pumped by the third harmonic (355 nm) of a Nd:YAG laser (Quanta Ray DCR-2(10)) was purified by a Glan air prism. The beam was then split into a weak beam (ω') and a strong beam (ω) by means of a conventional beam splitter. The intensity ratio of the strong beam compared to that of the weak beam was measured to be approximately 10 to 1. The two beams were then counterpropagated and focussed at the same point in a conventional multiphoton ionization (MPI) cell with two 75-mm focal length lenses.

The MPI cell was made out of a six-way stainless steel pipe with 2 1/4" diameter conflat flanges. Two of the opposing conflat flanges were fitted with UV quality BK-7 quartz windows which acted as entrance and exit windows for the laser beams. One of the other conflat flanges was fitted with a BNC connector. A thin wire was attached to the end of the BNC connector which could be biased positively or negatively in order to collect either electrons or ions. The wire was biased from +10 to +200 volts with no observable change in electron signal during the experiments. In order to maintain uniformity from one experiment to the next, the voltage was kept at +100 volts.

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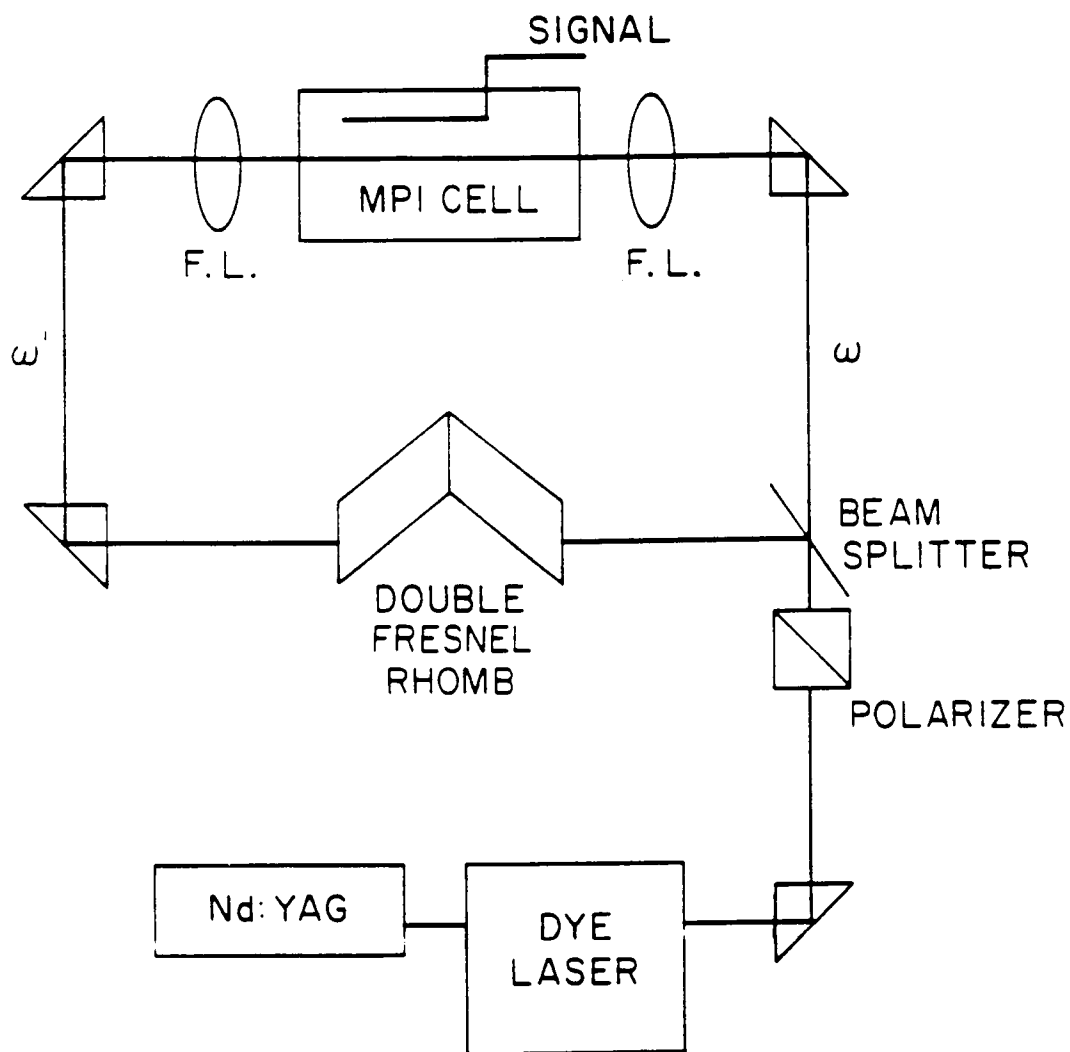


Figure II-2. Experimental setup for collisional m_j -mixing studies.

One conflat flange was fitted with a stainless steel pipe fitting and valve and used to pump and fill the MPI cell. The other conflats were solid. Xenon pressure was measured with a baratron pressure gauge.

The experiment utilizes the well known interference effect between three-photon excitation and third harmonic generation.⁹¹⁻⁹³ Figure II-3 shows the various excitation ionization pathways involving the two laser beams. Briefly, resonantly enhanced multiphoton ionization through the 3-photon excitation of the $6s[1/2]_1$, $6s'[1/2]_1$, $7s[3/2]_1$, and $5d[3/2]_1$ states of Xe is canceled above a certain pressure because of destructive interference between the 3-photon excitation process and the generated third harmonic VUV photon in the medium. In the counterpropagating arrangement, blocking the weak beam (ω') results in cancellation of the ionization signal. This demonstrates that excitation occurs primarily by absorption of two photons from the strong beam (ω) followed by the absorption of one or more photons from the counterpropagating weak beam (ω'). Ionization then occurs by the absorption of one or more photons from the strong beam. Third harmonic generation in the counterpropagating experiment is not possible due to phase matching considerations. Using two beams allows selective population of the $m_j=0,\pm 1$ magnetic sub-levels. When both beams are linearly polarized and parallel, then only the $m_j=0$ magnetic sub-level of the

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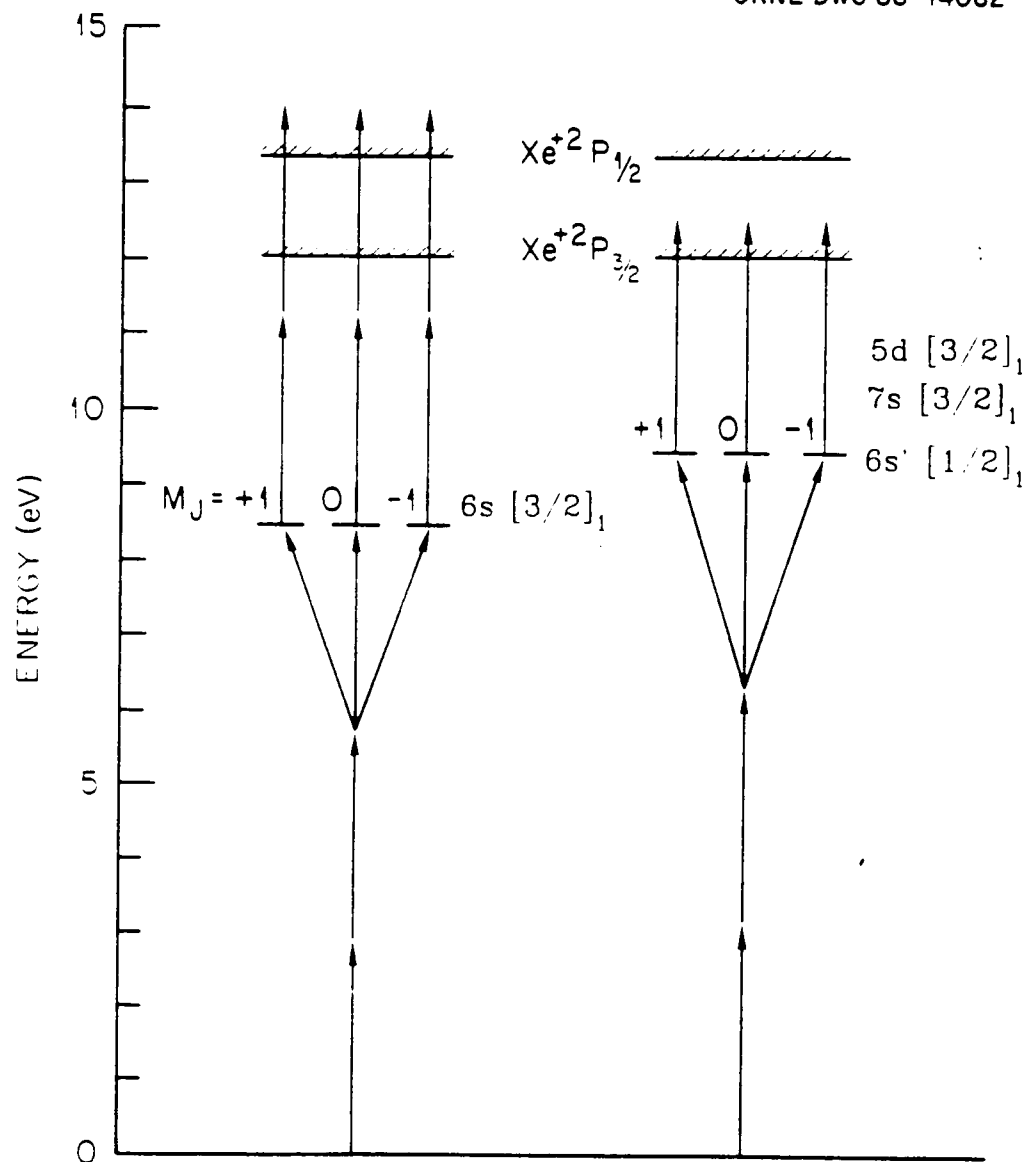


Figure II-3. Energy level diagram depicting three-photon resonant five-photon ionization of the $6s[3/2]_1$ state of xenon and the three-photon resonant four-photon ionization of the $6s'[1/2]_1$, $7s[3/2]_1$, and $5d[3/2]_1$ states of xenon.

excited state is populated, while only the $m_j = \pm 1$ magnetic sub-levels are populated when the planes of polarization of the two beams are perpendicular.³³

The plane of polarization of the weak beam was rotated by means of a double Fresnel rhomb. The double Fresnel rhomb was made out of high quality quartz with its center wavelength in the visible. The double Fresnel rhomb was connected to a stepping motor which allowed continuous rotation of the plane of polarization of the weak beam. The polarization of the weak beam was checked following the double Fresnel rhomb. The polarization was determined to remain >99% linearly polarized. In all cases, the measured ionization signal varied as $A + B \cos^2\theta$, where θ is the angle between the planes of polarization of the strong and weak beam.

Results and Discussion

Two ionization spectra taken in the wavelength range between 439 and 441 nm are shown in figure II-4. These spectra were taken using the counterpropagating arrangement shown in figure II-2. The spectrum labeled (I) was taken when the planes of polarizations of the beams were parallel. The spectrum labeled (II) was taken when the planes of polarizations of the two beams were perpendicular. As can

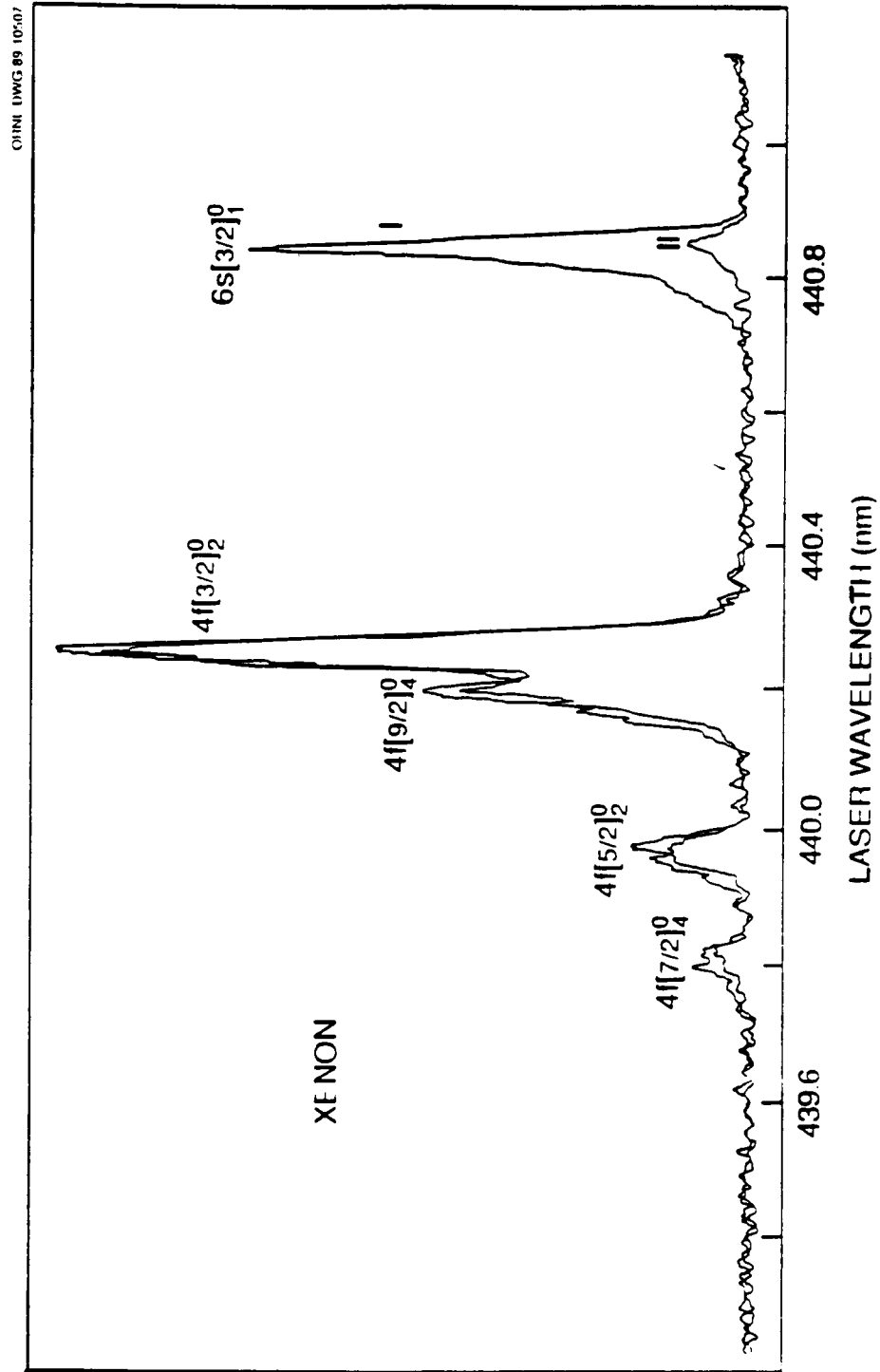


Figure II-4. Multiphoton ionization spectrum of xenon in the wavelength range 439-441nm for parallel (I) and perpendicular (II) polarizations of linearly polarized counterpropagating laser beams.

be seen from the two spectra, the ionization intensity through the 4f states does not change for the two different polarizations because excitation to the 4f states requires four photons. As a result, harmonic generation cannot occur and therefore no cancellation effect is observed. However, in the case of ionization through the $6s[3/2]_1$ state there is a dramatic difference in the ionization spectra between the two polarizations. The difference is easily understood by examining the ratio of the excitation probabilities of the $m_j=\pm 1$ sublevels to that of the $m_j=0$ sublevel and considering the ionization cross-sections of each of these sublevels.

The magnitude of three-photon excitation in a counterpropagating beam experiment can be expressed as a sum of all possible permutations of the polarizations of the laser beams:

$$\vec{P} = \vec{E}_1 \cdot \vec{E}_1 \cdot \vec{E}_2 + \vec{E}_1 \cdot \vec{E}_2 \cdot \vec{E}_1 + \vec{E}_2 \cdot \vec{E}_1 \cdot \vec{E}_1 . \quad (\text{II-1})$$

For parallel and perpendicular orientations of the polarization equation (II-1) reduces to

$$P_1 = E_1^2 E_2 + E_1^2 E_2 + E_1^2 E_2 \quad (\text{II-2})$$

and

$$P_1 = E_1^2 E_2 . \quad (\text{II-3})$$

Therefore, the ratio of the magnitudes is

$$\frac{P_{\perp}}{P_{\parallel}} = \frac{1}{3} \quad (\text{II-4})$$

and the excitation probability based on the polarization of the two laser beams is

$$\therefore S \approx \left(\frac{P_{\perp}}{P_{\parallel}}\right)^2 \approx \frac{1}{9} . \quad (\text{II-5})$$

Calculated ionization cross-sections from multichannel quantum defect theory for ionization from the m_j sublevels yield $0.33 \times 10^{-48} \text{ cm}^2 \text{ sec}$ and $0.45 \times 10^{-48} \text{ cm}^2 \text{ sec}$ for the $m_j = \pm 1$ and $m_j = 0$ sublevels, respectively.⁹⁴ Therefore, the ratio is calculated to be

$$R \approx \frac{S_{\perp}}{S_{\parallel}} \times \frac{\sigma_{m_j=\pm 1}}{\sigma_{m_j=0}} \times 2 \approx 0.16 , \quad (\text{II-6})$$

where S is the ionization signal for parallel and crossed polarizations of the counterpropagating beams and σ is the ionization cross-section from a particular m_j sublevel. The factor of 2 takes into account that there are two $|m_j|=1$ sublevels and only one $m_j=0$ sublevel. Collisional dephasing and disalignment are considered to be negligible at this pressure.

The dependence of the ionization intensity via the $6s[3/2]_1$ state as a function of the plane of polarization of the weak beam to that of the strong beam at 10 and 120 Torr is shown in figure II-5. The maxima correspond to parallel polarizations, while minima correspond to perpendicular

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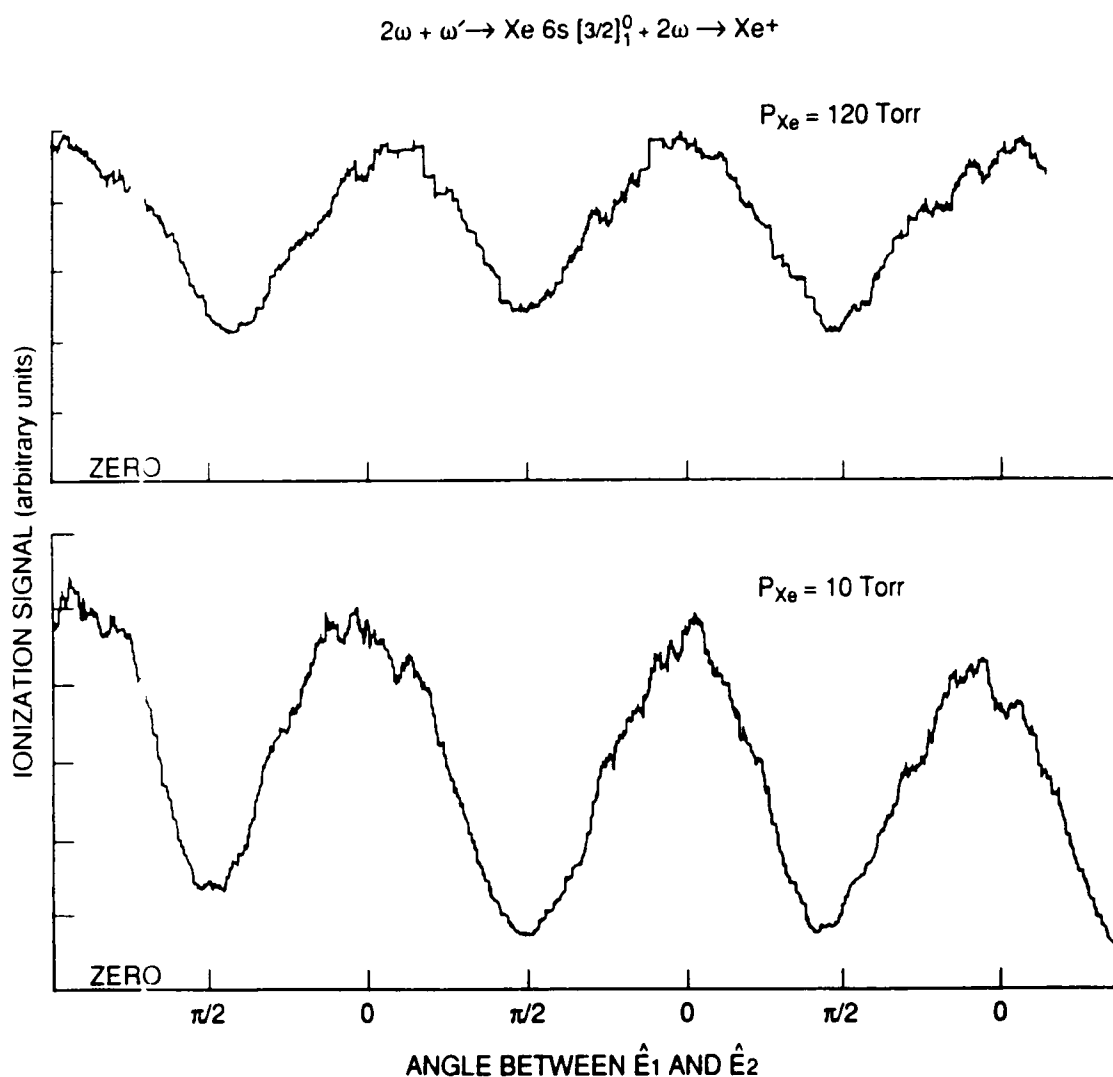


Figure II-5. Resonantly enhanced (3+2) multiphoton ionization signal via the $6s[3/2]_1^0$ state of xenon as a function of the angle between the electric field vectors of two linearly polarized counterpropagating beams at two different pressures.

polarizations. In all cases the intensity fits a $A + B\cos^2\theta$ function, where θ is the angle between the planes of polarizations of the two laser beams. From such graphs the ionization ratio, $R=P_1/P_0$, is extracted.

The dependence of the ionization intensity via the $6s' [1/2]_1$, $7s[3/2]_1$, and $5d[3/2]_1$ states as a function of the angle between the planes of polarization of the two laser beams show that R is independent of the pressure of the gas. The points in figure II-6 show the experimental results of the ionization ratio as a function of gas pressure for the $6s' [1/2]_1$ state. The experimental value of R is 0.21 (± 0.02) over the pressure range of 10 to 180 Torr. The solid line in figure II-6 displays the theoretically calculated value of R employing the model in this study ($R_{th}=0.22$). The $7s[3/2]_1$ and $5d[3/2]_1$ states exhibited similar pressure independence, $R=0.25$ (± 0.03) and $R=0.18$ (± 0.05), respectively. The reason for this pressure independence lies in the fact that ionization from these excited states requires only one photon. For the $6s' [1/2]_1$ state, MQDT calculations indicate that the ionization process is saturated at $2 \times 10^8 \text{ W/cm}^2$.⁹⁴ Therefore, within the experimental parameters employed, collisions do not occur fast enough to cause any dephasing or disalignment of the excited state. The constant value for the ionization ratio R simply reflects the ratio of the Rabi frequencies of the magnetic sublevels $m_j=0$ and $m_j=\pm 1$ of the excited state

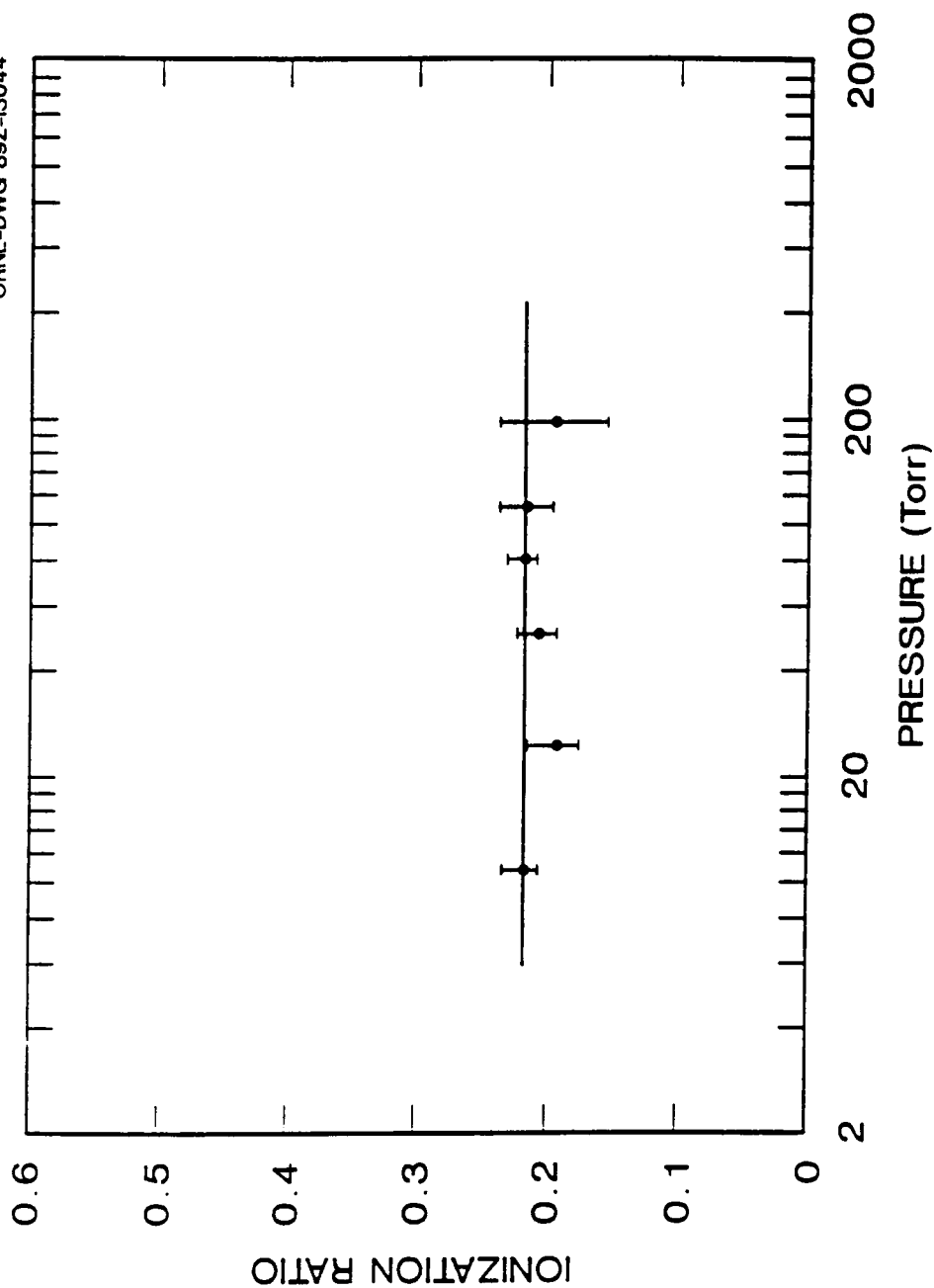


Figure II-6. Ionization ratio, R , vs. xenon pressure for resonantly enhanced (3+1) multiphoton ionization via the $6s'[1/2]_1$ state of xenon. Dots represent experimental data. Solid line represents theoretical curve with a constant value of $R=0.22$.

and is determined solely by the angular momentum.

For the $6s[3/2]_1$ state of xenon, which requires two more photons to ionize, the ratio R shows a obvious dependence on gas pressure within a certain range. The measured value of R versus the pressure is shown in figure II-7. At low pressures R increases from 0.13 (± 0.05) to 0.5 (± 0.04) at 130 Torr and does not exhibit any significant change from this value up to 190 Torr. The change in R as the gas pressure is increased is a result of population transfer between m_j levels due to elastic collisions between excited xenon atoms and xenon atoms in the ground state. Figure II-8 shows the relevant excitation and depopulation pathways of the m_j sublevels for resonantly enhanced (3+2) multiphoton ionization via the $6s[3/2]_1$ state. The levels are labeled as follows: $|0\rangle$ for the ground state, $|1\rangle$ for the $m_j=0$ magnetic sublevel, $|2\rangle$ for the $m_j=-1$, and $|3\rangle$ for the $m_j=1$ magnetic sublevels. When the counterpropagated beams are parallel, the $m_j=0$ magnetic sublevels are populated and as the pressure increases population is transferred to the $m_j=\pm 1$ magnetic sublevels. This results in a decrease in the ionization signal, since the ionization cross sections of the $m_j=\pm 1$ magnetic sublevels are smaller than that of the $m_j=0$ magnetic sublevel. Conversely, when the counterpropagated beams have perpendicular polarizations, the $m_j=\pm 1$ magnetic sublevels are populated. As the gas pressure is increased the ionization signal also

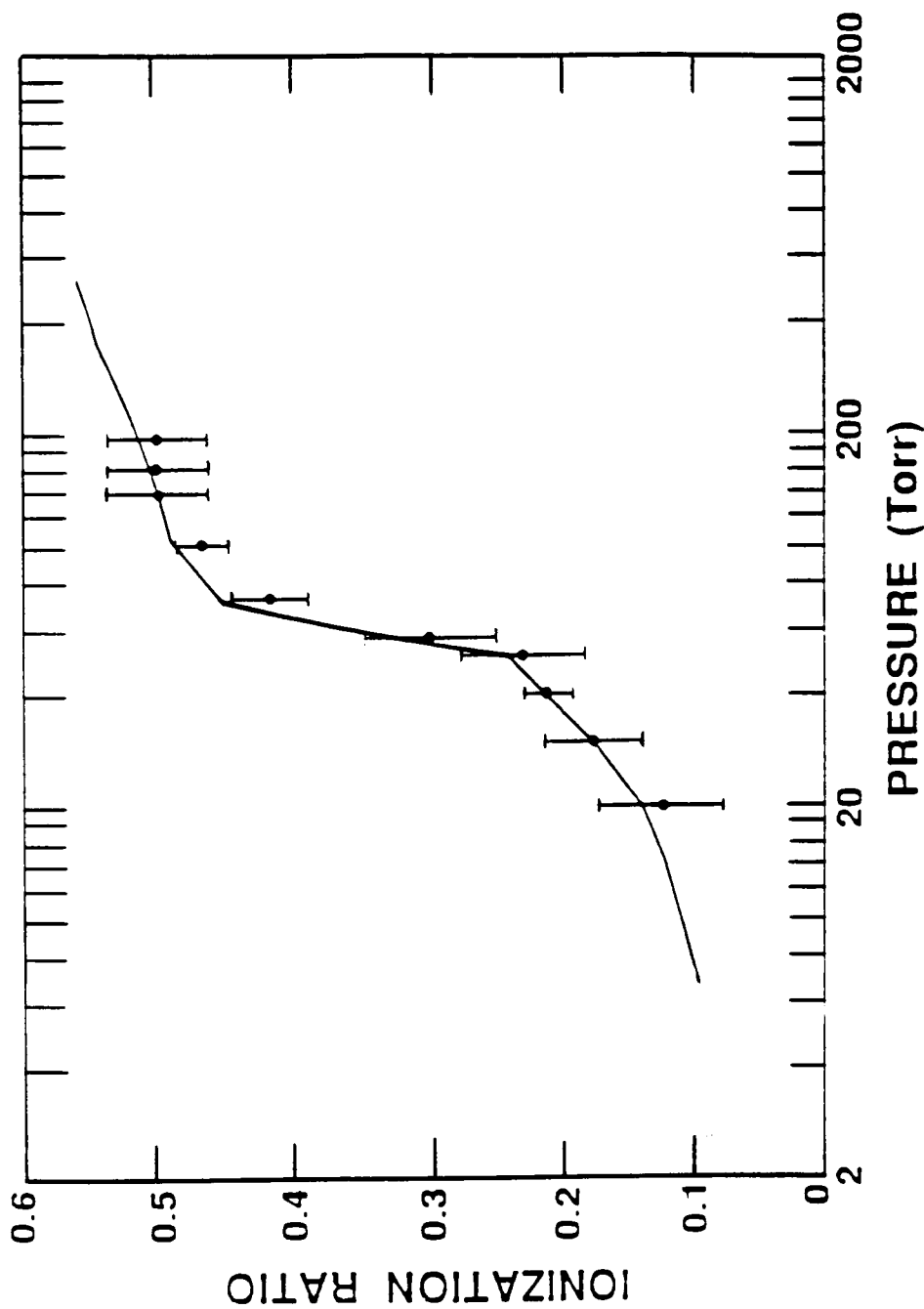


Figure II-7. Ionization ratio, R , vs. xenon pressure for resonantly enhanced (3+2) multiphoton ionization via the $6s[3/2]_1$ state of xenon. Dots represent experimental data. Solid line represents theoretical generated curve.

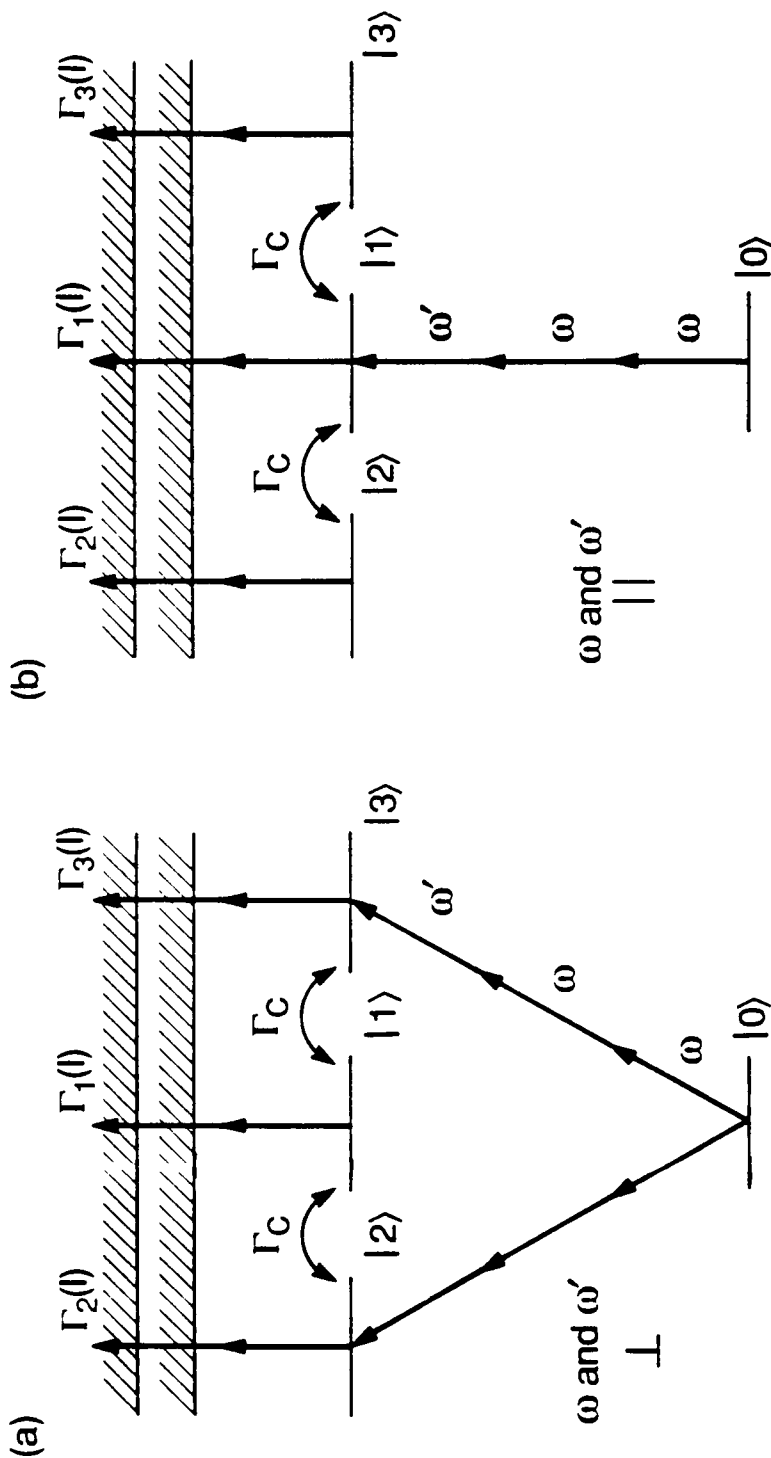


Figure II-8. Excitation and ionization pathways for resonantly enhanced (3+2) multiphoton ionization via the $6s[3/2]_1$ state of xenon. Selective population of magnetic sublevels is achieved by using parallel and perpendicular polarizations of linearly polarized counterpropagating laser beams. Γ_c indicates disalignment pathways.

increases due to population transfer to the $m_j=0$ magnetic sublevel where ionization is more efficient.

The change in R as a function of gas pressure represents an interplay between the different collisional processes. Thus an analysis of R can yield information on a number of different collisional processes. A system of rate equations (figure II-9), based on the density-matrix formalism,⁹⁵ can be used to describe the different collisional processes. p_a and p_e represent the two cases when the polarization of the two laser beams are parallel or perpendicular with respect to each other. When the beams are parallel, $p_a=1$ and $p_e=0$. When the beams are perpendicular, $p_a=0$ and $p_e=1$. Population transfer between m_j levels, due to elastic collisions, is represented by the rate constant $\Gamma^{(c)}$. The collisional rate constant is given by $\Gamma^{(c)}=N\langle v \rangle \sigma$, where N is the density of atoms, $\langle v \rangle$ is the mean relative velocity of the colliding atoms, and σ is the cross-section for a particular collision process. N is essentially the number of atoms in the ground state which depends linearly on pressure. Values for σ were obtained by solving the rate equations and fitting values for $\Gamma^{(c)}$. Theoretical analysis of the experiment was performed by P. Lambropoulos and X. Tang at the University of Southern California and A. Lyras at the Foundation for Research and Technology-Hellas, Crete. Only the results of the analysis will be given here. For more details concerning the

theoretical analysis the reader is referred to the paper by Charalambidis et al.⁹⁶

Basically, two types of collisional rate constants can be determined from this type of experiment. The first represents the rate at which population is transferred out of one m_j sublevel and into another during a collision. This process is known as collisional disalignment and is represented by $\Gamma^{(c)}_{s,s'}$ ($s, s' = 1, 2, 3; s \neq s'$) in the set of rate equations. s indicates the relevant bound state (see figure II-8).

The other type of rate constant represents the various collisional dephasing mechanisms that compete with collisional disalignment. Dephasing is the loss of coherence between the excited state and the ground state represented by the Rabi frequency (Ω_{0s} ($s=1, 2, 3$)). The dephasing or collisional relaxation rate constants are represented by $\Gamma^{(c)}_{s,0}$ ($s=1, 2, 3$) in figure II-9.

Three types of dephasing mechanisms are considered in the analysis. The first involves the removal of an atom from the excited state thereby destroying the coherence between the ground and excited state. This type of dephasing mechanism is known as ionization and is represented by $\Gamma^{(i)}_s$ ($s=1, 2, 3$) in the set of rate equations. For the $6s[3/2]_1$ state, ionization is very weak, so the collisional rate constant for ionization is small compared to the other dephasing mechanisms.

$$\dot{\rho}_{00} = \frac{\Omega_{01}^2}{\gamma_1}(\rho_{11} - \rho_{00})pe + \left[\frac{\Omega_{02}^2}{\gamma_2}(\rho_{22} - \rho_{00}) + \frac{\Omega_{03}^2}{\gamma_3}(\rho_{33} - \rho_{00}) \right]pa$$

$$\dot{\rho}_{11} = -\left(\Gamma_1^{(I)} + \Gamma_1^{(c)}\right)\rho_{11} + \Gamma_{21}^{(c)}\rho_{22} + \Gamma_{31}^{(c)}\rho_{33} - \frac{\Omega_{01}^2}{\gamma_1}(\rho_{11} - \rho_{00})pe$$

$$\dot{\rho}_{22} = -\left(\Gamma_2^{(I)} + \Gamma_2^{(c)}\right)\rho_{22} + \frac{\Gamma_1^{(c)}}{2}\rho_{11} + \Gamma_{32}^{(c)}\rho_{33} - \frac{\Omega_{02}^2}{\gamma_2}(\rho_{22} - \rho_{00})pa$$

$$\dot{\rho}_{33} = -\left(\Gamma_3^{(I)} + \Gamma_3^{(c)}\right)\rho_{33} + \frac{\Gamma_1^{(c)}}{2}\rho_{11} + \Gamma_{23}^{(c)}\rho_{22} - \frac{\Omega_{03}^2}{\gamma_3}(\rho_{33} - \rho_{00})pa$$

Figure II-9. Rate equations which describe collisional disalignment and dephasing. pa and pe represent parallel and perpendicular polarizations of the two laser beams with respect to one another; when the two beams are parallel, pa = 1 and pe = 0; when they are perpendicular, pa = 0 and pe = 1. Ω represents the three-photon Rabi frequency for excitation from the ground state the three degenerate magnetic sublevels. Γ represents the collisional rate constants. γ represents the combination of diagonal and off-diagonal relaxation constants.

The second dephasing mechanism arises from fluctuations in the laser field. Fluctuations in the field results in loss of coherence between the ground and the excited state established by the field. At low pressures this dephasing mechanism dominates. The third mechanism involves the interruption of the phase coherence in the excited state as a result of collisions. Such a collision produces a virtual state that is a superposition of the degenerate m_j sublevels. At higher gas pressures, where the ratio R changes, collisional dephasing dominates over the other dephasing mechanisms.

The solid line in figure II-7 represents the theoretical curve obtained by solving the rate equations and adjusting to the experimental data by varying the collisional relaxation rate constants. In order to theoretically reproduce the experimental data, the ratio of the collisional relaxation rate constants was taken to be $\Gamma^{(c)}_{s0}/\Gamma^{(c)}_{10}=7$ ($s=2,3$) and the ratio of the dephasing rate to the rate of disalignment was taken to be $\Gamma^{(c)}_{10}/\Gamma^{(c)}_1=60$. The former ratio indicates that ground state atoms have a larger collisional cross section with $m_j=0$ levels than with $|m_j|=1$ levels, while the latter ratio shows that only a small fraction of the collisions produce an excited state with a definite m_j . From these values of $\Gamma^{(c)}$, a cross-section for disalignment of the $6s[3/2]_1$ from the $m_j=0$ sublevel to each of the $|m_j|=1$ sublevels was calculated to be of the order

of $10\text{\AA}^2$ and estimated to be 100 times larger than the largest ionization rate. The total collisional cross-section of Xe 6s atoms in the $|m_j|=1$ state with ground state atoms was calculated to be $600\text{\AA}^2$. The corresponding cross section for Xe 6s $m_j=0$ atoms was calculated to be seven times larger.

Although, to the best of our knowledge, no other values of collisional disalignment cross sections for the $6s[3/2]_1$ state in xenon are known to exist, the values obtained here are in reasonable agreement with the work of Husson and Magerie⁹⁷ and Suzuki and Shimoda.⁸⁶ They measured the disalignment cross sections for the $6p[1/2]_1$, $6p[3/2]_2$, and $5d[5/2]_3$ states of xenon colliding with other xenon atoms. The techniques used were a pulsed electron beam method and Hanle effect method, respectively.

In summary, this study has presented a new method to probe collisional interactions between state-selected and ground-state atoms using resonantly enhanced multiphoton ionization. A limitation of the method is that the total angular momentum of the excited state must differ from the ground state by one so that harmonic generation is possible. However, circularly polarized light can be used in which case the only restriction is that the total angular momentum of the excited state be high enough so that the selection rule, $\Delta m_j = \pm 1$ be satisfied. An obvious advantage of this method is that elaborate apparatus calibrations are avoided

since the measurement involves a relative quantity not an absolute one. This method can also be extended in a number of different directions that include examination of collisional interactions with other types of gases, the effect of laser intensity, and the effect of relative phase shifts between the two counterpropagating beams on the ionization signal.

Chapter III

Multiphoton Ionization Photoelectron Spectroscopy

Introduction

The technique of monitoring the kinetic energy of an electron that is ejected as a result of the collision of a photon with an atom or molecule is known as photoelectron spectroscopy. Photoelectron spectroscopy (PES) has developed into a mature and important field in chemistry and physics providing an abundance of information on the ionization potentials, ionization cross sections, transition probabilities, etc., of various atomic and molecular systems. Its development has been essentially accredited to K. Siegbahn.⁹⁸ The general principles and applications have been reviewed⁹⁹ by a number of authors as well as numerous works devoted to tabulation of PES data.¹⁰⁰

Generally, PES can be considered to consist of two subfields based on the type of radiation used as an ionization source: X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS). XPS experiments are usually concerned with the ionization of core electrons of atoms or molecules due to the high energy photons involved. Intrinsically, the resolution in XPS

experiments is poor. UPS experiments employ ionization sources that are less energetic than in XPS and are usually limited to determining binding energies of valence electrons in atoms and molecules and examining the vibrational and rotational structure of the resulting molecular ions. A typical source of radiation used in UPS experiments is the He(I) line (21.22 eV). In recent years, synchrotron radiation has been used as a tunable radiation source in PES experiments to study the photoionization dynamics as a function of photon energy.

XPS and UPS are both single-photon ionization techniques, i. e., ionization occurs in a single transition from the ground state of an atom or molecule into the continuum. The end result is the formation of a positive ion and a free electron. Most of the dynamical information concerning the ionization process is carried off by the photoejected electron. From conservation of energy the kinetic energy of an electron ejected from an atom is

$$K.E. = \hbar\omega - I.P., \quad (III-1)$$

where I. P. is the ionization potential of the atomic system and $\hbar\omega$ is the energy of the impinging photon. For a molecular system the kinetic energy of a photoejected electron is

$$K.E. = \hbar\omega - I.P. - E_{vib} - E_{rot}, \quad (III-2)$$

where E_{vib} and E_{rot} are the energies of the vibrational and

rotational levels of the various ionic electronic states. A shortcoming of these techniques is that no information about intermediate excited states below the first ionization threshold can be ascertained. Studies are limited to the ground state. Single-photon excitation to intermediate levels followed by absorption of another photon for ionization is not possible with the radiation sources used in conventional PES because of the low power densities associated with them. The advent of the laser, and the field of non-linear spectroscopy, surmounts this shortcoming. Using the laser as a radiation source, multiphoton excitation of an excited state is possible with visible light. In addition, excited states that are forbidden in one photon may be excited by the absorption of two or more photons. Combining non-linear spectroscopy and PES creates a new and powerful technique for studying the photoionization dynamics from the excited states of atoms and molecules. This technique is known as multiphoton ionization photoelectron spectroscopy (MPI-PES).

In general, two types of experiments are carried out in MPI-PES experiments. The first involves scanning the laser wavelength and monitoring the ions or electrons produced. This allows for location of intermediate levels due to the increase in the ion or electron signal as a result of resonant enhancement in the excitation process. The second involves setting the wavelength of the laser on one of these

resonances and monitoring the kinetic energy of the photoemitted electrons. Kinetic energy analysis yields essentially the same dynamical information as conventional PES. MPI-PES, however is a much more powerful technique. Interpretation of molecular MPI-PES spectra should be easier than conventional PES spectra due to the lack of congestion. This lack of congestion arises from the fact that ionization occurs from a Rydberg state. A Rydberg state has a geometry similar to that of the ion. From the Franck-Condon principle, the vibrational quantum number is not expected to change in the ionization process. The PES spectrum will consist of only one peak corresponding to $\Delta v=0$. As always, deviations can occur in which this propensity rule breaks down (e. g. Rydberg valence interactions¹⁰¹).

Measuring the photoelectron signal as a function of the angle between the photoejected electron and the polarization vector can provide even more information about the excited intermediate state. In conventional, one-photon ionization, Cooper and Zare¹⁰² have shown that the differential cross section from any isotropic ground state has the form

$$\frac{d\sigma}{d\Omega} = I(\theta) = \frac{\sigma_{TOTAL}}{4\pi} [1 + \beta P_2(\cos\theta)], \quad (III-3)$$

where σ_{TOTAL} is the total ionization cross section and $P_2(\cos\theta)$ is the second-order Legendre polynomial ($P_2 = [(3/2)\cos^2\theta - (1/2)]$). β is the asymmetry parameter which determines the shape of the angular distribution. Note that

the total ionization cross section can be determined simply by measuring the photoelectron intensity at an angle where $P_2(\cos\theta)$ vanishes i. e., $\theta = \cos^{-1} 1/\sqrt{3} = 54.7$ degrees. β is defined by

$$\beta = \frac{\ell(\ell-1)R_{\ell-1}^2 + (\ell+1)(\ell+2)R_{\ell+1}^2 - 6\ell(\ell+1)R_{\ell+1}R_{\ell-1}\cos\delta}{(2\ell+1)[\ell R_{\ell-1}^2 + (\ell+1)R_{\ell+1}^2]} \quad (\text{III-4})$$

where $R_{\ell=\pm 1}$ are the radial matrix elements between the bound and continuum wave functions of the outgoing partial waves and δ is the difference in the phase shifts of the outgoing partial waves. Within the electric-dipole approximation the selection rule on the angular momentum of the outgoing electron is $\Delta\ell=\pm 1$. Hence, ionization of an electron with $\ell \neq 0$ can lead to two different outgoing waves. These two outgoing waves can interfere with one another. Single-photon ionization from a pure s orbital leads to a single p-partial outgoing wave. Thus, $\delta=0$ and according to equation III-3 above, the photoelectron angular distribution will exhibit a pure $\cos^2\theta$ distribution. For ionization from a non s orbital, $\delta \neq 0$, the shape of the angular distribution will depend on the type of interference between the two outgoing waves. Therefore, the differential cross section β can take on values from +2 ($\cos^2\theta$ distribution) through 0 (isotropic distribution) to -1 ($\sin^2\theta$ distribution). However, relativistic interactions can play a role in the photoionization process and produce dramatic effects on the photoelectron angular distribution.^{103,104}

The first measured photoelectron angular distribution employing ultraviolet radiation as an ionization source was performed by Chaffee¹⁰⁵ in 1931. The experiment involved the ejection of a 4s valence electron from potassium. The obtained angular distribution was proportional to $A + B\cos^2\theta$ as predicted by equation III-3. In a multiphoton ionization process, the angular distribution measures the anisotropy introduced with the absorption of each photon and reflects the nature of the orbital of the excited state from which the electron is ejected. A more general form of the differential cross section is then needed. The angular distribution is expressed as an expansion of Legendre polynomials up to order $2N$ where N is the number of photons needed to ionize and has the form

$$\frac{d\sigma^{(N)}}{d\Omega} = \frac{\sigma_{TOT}^{(N)}}{4\pi} \sum_{i=0}^N \beta_{2i} P_{2i}(\cos\theta), \quad (\text{III-5})$$

where $\sigma_{TOT}^{(N)}$ is the N -photon cross section and $P_{2i}(\cos\theta)$ is the $2i$ th order Legendre polynomial. Higher order terms are needed to reflect the degree of alignment of the total angular momentum of the intermediate state. A comparable general expression of angular distributions involving the products of nuclear reactions, in particular β and γ decay, was first predicted by Wang.¹⁰⁶ The first calculation of an angular distribution for a MPI process was carried out by Zernik for non-resonant two-photon ionization from the

metastable 2s state of atomic hydrogen.¹⁰⁷ Tully et al.¹⁰⁸ investigated angular distributions of photoelectrons that resulted from two-photon ionization of molecules.

Theoretical analysis of angular distributions for a resonant two-photon ionization process was first conducted by M. Lambropoulos and Berry¹⁰⁹ for photoionization from the $3p^2P_{1/2}$ and $3p^2P_{3/2}$ excited states of sodium. The first multiphoton photoelectron angular distribution experiment was performed by Edelstein et al.¹¹⁰ in 1974. They measured the photoelectron angular distribution of a resonant two photon ionization process via the X^3G_5 excited state of titanium. The data was taken by measuring the photoelectron current at six different angles by rotating the polarization of the nitrogen laser with a half-waveplate. The ion was left in the 4F_J state in any one of four possible J sublevels. Unfortunately, Edelstein et al. were unable to distinguish between the four final ionic states. The resulting angular distribution was nearly isotropic with the contribution of each state canceling each other. Although interpretation of the results for this resonant process was excessively complex, due to the nature of Ti, the experiment did prove the feasibility of the technique to investigate the nature of excited states in atoms. From these initial studies an avalanche of others soon followed.

Compton et al.¹¹¹ performed the first resonantly enhanced MPI-PES experiment. These authors measured the

photoelectron energy distributions that resulted from multiphoton ionization of xenon via the $6s[3/2]_1$, $6s'[1/2]_1$, and $5d[3/2]_1$ excited states. They reported that resonantly enhanced (3+2) MPI via the $6s[3/2]_1$ state results in Xe^+ in both the $^2P_{1/2}$ and $^2P_{3/2}$ final states.

Miller and Compton¹¹² also performed the first resonantly enhanced MPI-PES experiment on a molecule. They investigated resonantly enhanced (2+2) MPI through the various vibrational levels of the A $^2\Sigma^+$ and C $^2\Pi$ electronic states of nitric oxide. The photoelectron energy spectra were governed by Franck-Condon factors between the two-photon intermediate Rydberg state and the ion. The resulting NO^+ was produced in the same vibrational state as the Rydberg intermediate, i. e., $\Delta v=0$. They also reported the observation of slow or "zero" energy electrons while investigating resonantly enhanced (2+2) MPI via the A $^2\Sigma^+$ state of NO.

Miller and Compton¹¹³ measured the photoelectron and mass resolved ion kinetic energies from resonantly enhanced MPI of iodine showing the viability of resonantly enhanced MPI-PES in determining fragmentation mechanisms in molecules.

Investigating the six-photon non-resonant multiphoton ionization of xenon, Agostini et al.¹¹⁴ reported the observation of photoelectrons that had energy which corresponded to the absorption of an additional photon above

the ionization threshold. The absorption of the seventh-photon was explained by the authors in a two-step, inverse bremsstrahlung model where the atom is first ionized and then the resulting electron absorbs photons in the presence of the potential of a nearby ion.

Gontier et al.¹¹⁵ reexamined the inverse bremsstrahlung model for this "continuum-continuum" transition and presented a second model in which the electron undergoes a transition from the ground state of the atom to the final continuum state via virtual intermediate states. They called this single-step process "above threshold ionization" (ATI). Although initial comparison of the ATI model with results by Agostini et al. showed rather poor agreement, Gontier and Trahin¹¹⁶ later showed, based on an ATI model of hydrogen, that the experimental results of Agostini et al. are more suitably explained by the ATI model rather than the inverse bremsstrahlung because the laser pulse is shorter than the collision time.

Some other models that have been used to explain ATI have involved pondermotive effects¹¹⁷ and inverse half-bremsstrahlung.¹¹⁸

Since the discovery of the "continuum-continuum" transitions, by Agostini et al. in 1979, a considerable amount of theoretical and experimental work has been performed. Agostini et al.¹¹⁹ reported the observation up to four additional photons than the six required for the

ionization of xenon using the second harmonic of the YAG. They measured the polarization dependence at 0° and 90° for photoelectrons that resulted from leaving either ion core of Xe^+ showing that the dependence was different for leaving the two ion cores. Fabre et al.¹²⁰ showed that the measured photoelectron angular distribution for leaving the $^2\text{P}_{3/2}$ ion core was different for ATI electrons than for electrons from six-photon ionization.

Kruit et al.¹²¹ measured the angular distributions of the photoelectrons from five-photon ionization and (5+1) photon ionization of xenon via an ac Stark shift into an intermediate state. The ac Stark shift resonance provides a means to accurately measure the laser intensity and thereby allow for a reliable comparison with theoretical models.

A review of early theoretical and experimental work on ATI has been compiled by Cooke and McIlrath.¹²² More recent experimental studies on ATI have involved the use of circularly polarized light¹²³⁻¹²⁶ and elliptically polarized light.¹²⁷

The effect of laser power on the angular distribution has been examined theoretically by Dixit and Lambropoulos^{128,129} and by Tang et al.¹³⁰ for extremely high laser fields. Distributions arising from two- and three-photon ionization in the autoionization region between the two thresholds in rare gases have also been theoretically investigated.¹³¹

Analysis of the influence of hyperfine splitting of the excited state on the measured angular distribution has been explored for cases of resonantly enhanced two-photon ionization of the alkalis.¹³²⁻¹³⁶ It was shown that if the hyperfine coupling is on the order of the laser pulse length the anisotropy of the excited state can be destroyed.

Dodhy et al.¹³⁷ measured photoelectron angular distributions for nonresonant two-photon ionization of cesium and rubidium. In the same study, they also reported results for above threshold ionization in cesium. Later, Dodhy et al.¹³⁸ investigated photoelectron angular distributions that resulted from a quadrupole transition in rubidium. Angular distributions were also reported for the first and second above threshold ionization photoelectron signals via the same quadrupole transition. Photoelectron angular distributions for two-photon resonant three-photon ionization of cesium, rubidium, and sodium has also been reported.¹³⁹

MPI-PES studies have also been conducted on the alkaline earths. Strong angular correction effects were investigated by Mullins et al. in barium.^{140,141} Sander et al.¹⁴² investigated angular distributions obtained from exciting autoionizing levels in barium. A review of the general subject of angular correlation in multiphoton ionization of atoms is given by Smith and Leuchs.¹⁴³

Photoelectron angular distributions were also measured

for resonantly enhanced MPI from autoionizing levels in krypton and xenon.^{144,145}

A number of reviews covering the fundamentals of MPI-PES as well as extensive listing of experimental studies have been published.¹⁴⁶⁻¹⁴⁹ The reader is referred to these publications for more information.

Experimental

A schematic of the experimental apparatus used to obtain photoelectron energy spectra and angular distributions is shown in figure III-1. The output of a pulsed, tunable dye laser (Quanta-Ray PDL-2) pumped by the second harmonic (532 nm) of a Nd:YAG laser (Quanta-Ray DCR-2(10)) was frequency doubled either by an Inrad autotracking frequency doubler (model 5-12) or a Quanta-Ray wavelength extender (WEX-1). The resulting UV light was focussed with a 38mm focal length lens into a vacuum chamber and intersected the sample gas beam which was introduced into the chamber via a pulsed nozzle (Lasertechnics Inc.) to conduct (3+1) and (3+2) resonantly enhanced MPI-PES studies on atoms and molecules. The ion signal was periodically monitored by means of a simple home-built linear time-of-flight mass spectrometer. No dimer ions were detected. In the (2+1) resonantly enhanced MPI-PES studies, the frequency

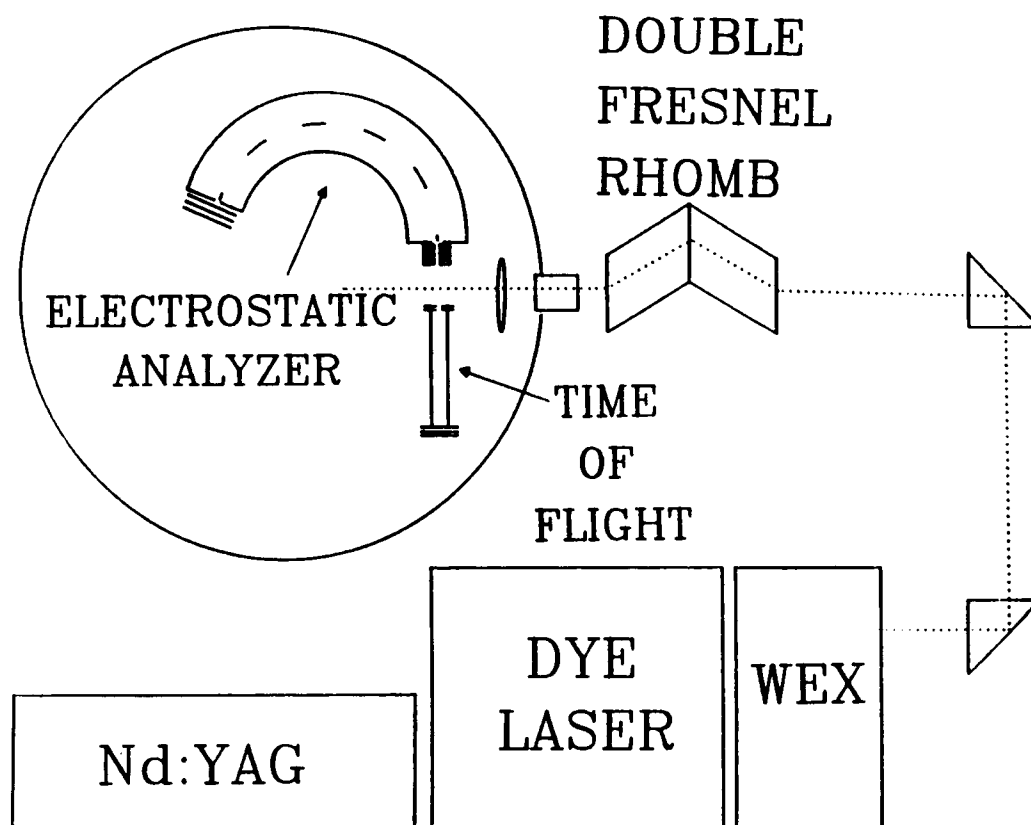


Figure III-1. Schematic of experimental apparatus used in resonantly enhanced multiphoton photoelectron studies.

doubled light was mixed with the fundamental of the Nd:YAG (1.064 μ m) and then focussed into the vacuum chamber.

The photoemitted electrons were monitored by means of a double-focussing 160° spherical-sector electrostatic energy analyzer with a mean radius, R_0 , of 2.874", constructed out oxygen free copper and sprayed with colloidal graphite (Aerodag) to eliminate surface patch potentials and to eliminate scattered electrons. The electrostatic analyzer was housed in a aluminum box that also was sprayed with colloidal graphite.

The analyzer was operated in a constant transmission energy mode. The transmission energy, E , given by

$$E = \frac{\Delta V}{r_1/r_2 - r_2/r_1} \quad (\text{III-6})$$

was determined by the radii of the outer (r_1) and inner (r_2) spheres of the analyzer and the voltage difference (ΔV) across them. For $r_1=3.186"$ and $r_2=2.562"$, equation III-6 reduces to

$$E = 2.276 \Delta V . \quad (\text{III-7})$$

In these experiments ΔV was typically set at 10 V. Therefore, only electrons with an energy of 22.76 eV were allowed to pass through the analyzer. Electrons entering the electrostatic energy analyzer were accelerated or de-accelerated to 22.76 eV by biasing the entire analyzer assembly. A photoelectron energy spectrum was obtained by

scanning the biasing voltage.

Photoelectrons emerging from the analyzer strike a dual microchannel plate assembly whereupon the signal is preamplified and averaged using a boxcar averager (PAR model 165). The averaged output is then plotted on an X-Y recorder.

The theoretical energy resolution is given by

$$\Delta E_{1/2} = \frac{Es}{2R_0} \quad (\text{III-8})$$

where R_0 is the mean radius of the electrostatic analyzer and s is the effective entrance and exit slit apertures. The effective entrance and exit slit apertures were 0.008". The theoretical resolution for this energy analyzer is then ~0.03 eV. Experimentally, poorer energy resolution was observed, ~0.175 eV, due to space charge effects as shown in figure III-2. Space charge arises from the mutual repulsion of electrons in the resulting electron beam. The maximum amount of current that can be transmitted is given by¹⁵⁰

$$I_{MAX} = 38.5 E^{3/2} (s^2/d^2) \quad (\text{III-9})$$

where I_{MAX} is in μA , d is the distance between the entrance and exit slits, s is the diameter of the exit and entrance slits, and E is the theoretical resolution. The theoretical maximum current that can be passed through the analyzer in the absence of space charge is calculated to be 4×10^{-9} A. With the signals observed, the currents are estimated to be around 2.3×10^{-8} A.

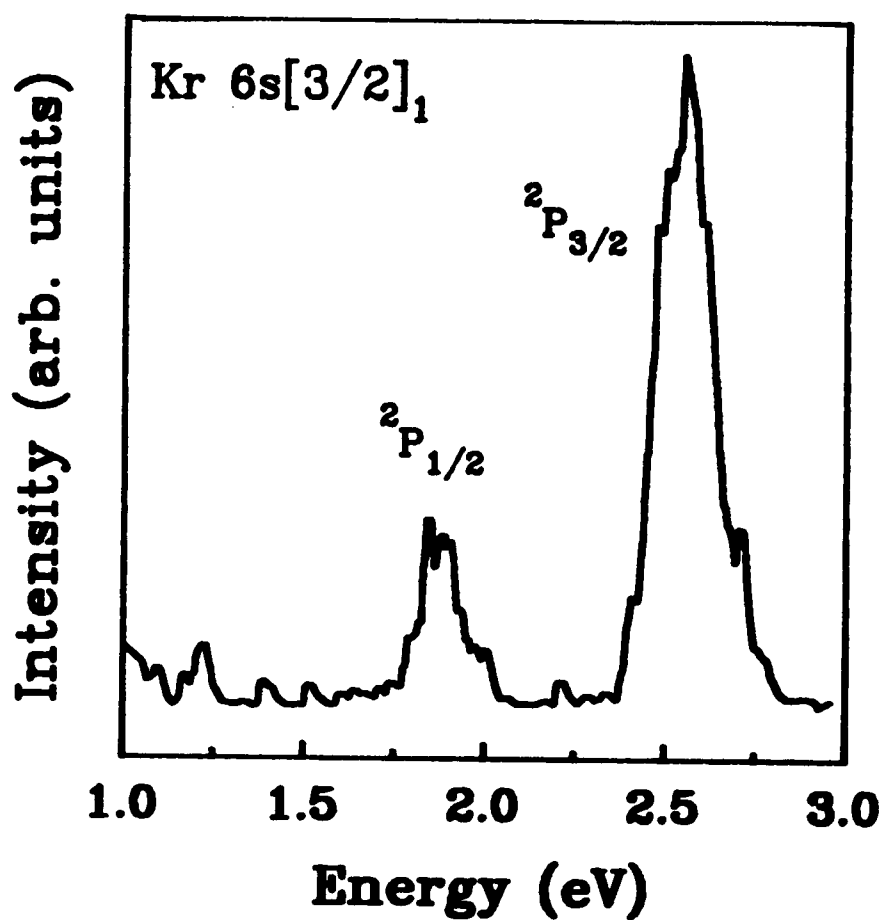


Figure III-2. Photoelectron energy spectrum that results from (3+1) resonantly enhanced MPI via the 6s[3/2]₁ state of krypton. FWHM = 0.175 eV.

The angular resolution of the electrostatic energy analyzer is defined by the size of the entrance slit in the grounded box housing of the energy analyzer and the distance to the focal spot of the laser beam (s/d). For a 0.5 mm aperture and a distance of 2 cm the theoretical angular resolution was determined to be $\pm 1.5^\circ$. A useful general method of calculating the trajectories of charged particles through an electrostatic analyzer employed in this study has been given by DeSerio.¹⁵¹

An einzel lens was used to image electrons emerging through the entrance aperture into the electrostatic analyzer. An einzel lens is a three electrode electrostatic lens in which the potential of the outer two electrodes are the same ($V_1=V_3$). The center electrode, V_2 , has a variable potential applied in order to focus the electrons into the electrostatic energy analyzer.

Each einzel lens electrode was 0.438" in diameter and 0.122" in length. They were made out of hard copper and had a 0.150" aperture drilled through the center. Sapphire spacers (0.063") were used to separate the electrodes. The einzel lens was mounted on a threaded plate which was able to be screwed directly on the electrostatic energy analyzer assembly.

Figure III-3 show a schematic of the einzel lens used in these experiments along with some calculated photoelectron trajectories for electrons with 1 eV of

THREE ELEMENT EINZEL LENS

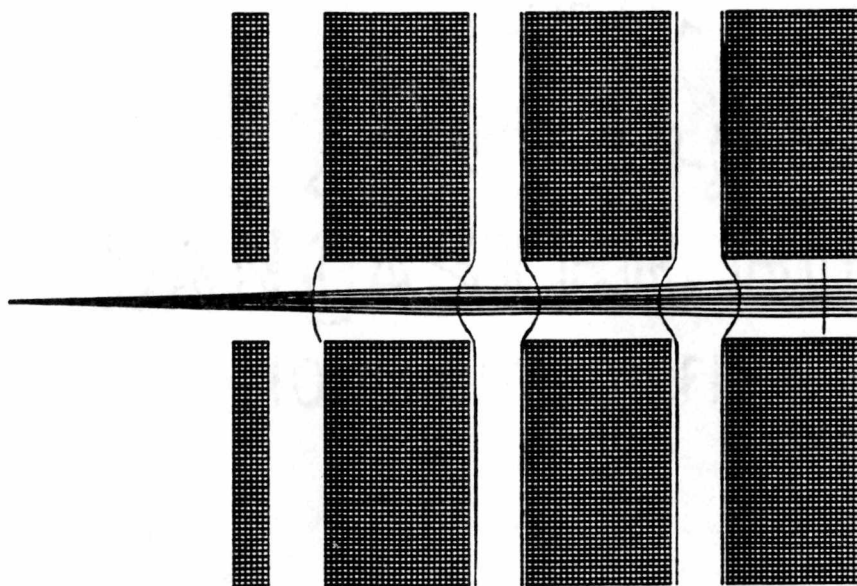


Figure III-3. Schematic of three element einzel lens. One eV photoelectrons are focussed into the electrostatic energy analyzer. The applied potential on the two outer electrodes is 21.76 V. The potential on the center electrode is 23.0 V.

energy. The voltage on the outer electrodes is 21.76 V and the voltage on the center electrode is 23.00 V.

Other than increasing the electron signal, the use of an einzel lens was found to have no effect on the energy or angular distributions of the photoemitted electrons. Angular distributions recorded with or without the einzel lens were identical except for intensity of the signal. Photoelectron angular distributions were recorded by tuning the electrostatic analyzer to the photoelectron signal and monitoring the electron signal as the plane of polarization of the doubled or doubled + $1.064\mu\text{m}$ light was rotated with a double fresnel rhomb. The double fresnel rhomb was made of calcium fluoride in order to operate at the short wavelengths employed in these studies ($220\text{nm} \leq \lambda \leq 340\text{nm}$). The angular distributions were recorded by continuously rotating the rhombs using a stepping motor. Angular distribution data is averaged over 2π and plotted from $0\sim\pi$ in the figures. A least-squares fit of the data is performed using a curve fitting routine to equation III-5, given by Bevington¹⁵² and presented in the figures as a solid line.

Results and Discussion

Atoms

Calculation of the photoelectron angular distributions reported for krypton and xenon were performed by Xian Tang and Peter Lambropoulos at the University of Southern California. The calculations are based on the multi-channel quantum defect theory (MQDT) formalism.^{153,154} MQDT is based on the fact that a Rydberg electron moves outside the core of the atom under the influence of the core Coulombic potential. The effect of short-range interactions between the electron and core can be described by a small number of parameters slowly varying with energy. All of the MQDT parameters for the $J=0,2$ even parity and $J=1,3$ odd parity Rydberg states were determined using the semiempirical method and results of ref. 153. MQDT generated angular distributions are presented as dashed lines in the figures.

Argon. A preliminary study of resonantly enhanced multiphoton ionization via the $4s[3/2]_1$ and $4s'[1/2]_1$ states of argon was conducted. Pressure dependence studies of the MPI spectra of argon in a cell have been previously investigated by Johnson et al.^{155,156} In this work, the kinetic energies of the photoemitted electrons were measured.

Excitation of the $4s[3/2]_1$ and $4s'[1/2]_1$ requires the

absorption of three photons. Figure III-4 shows the energy level diagram depicting the one- and two-photon ionization from the $4s[3/2]_1$ and $4s'[1/2]_1$ states, respectively. For the case of three-photon excitation of the $4s[3/2]_1$ state, an interesting near resonance occurs at the fourth photon. The energy of the fourth photon from the $4s[3/2]_1$ lies approximately 70 cm^{-1} below an allowed transition to the $9p[3/2]_2$ state. Thus, (3+2) resonantly enhanced MPI via the $4s[3/2]_1$ state is expected to be further enhanced at the four photon level as a result of the proximity of the $9p[3/2]_2$ state.

Figure III-5 shows the excitation spectra for the $4s[3/2]_1$ and $4s'[1/2]_1$ states. The excitation spectra were taken by placing the gate of the boxcar on the Ar^+ mass signal in the time-of-flight mass spectrum and tuning the dye laser. Figure III-5a shows a somewhat broader signal with two peaks. The first peak corresponds to resonantly enhanced (3+2) MPI via the $4s[3/2]_1$ state while the second peak to higher energy corresponds to resonantly enhanced (4+1) MPI via the $9p[3/2]_2$. Figure III-5b shows a single sharp peak which corresponds to resonantly enhanced (3+1) MPI via the $4s'[1/2]_1$ state.

Energy analysis of the photoemitted electrons show that resonantly enhanced (3+2) MPI via the $4s[3/2]_1$ state produces only one group of photoelectrons. The electrons were accelerated into the electrostatic analyzer with an

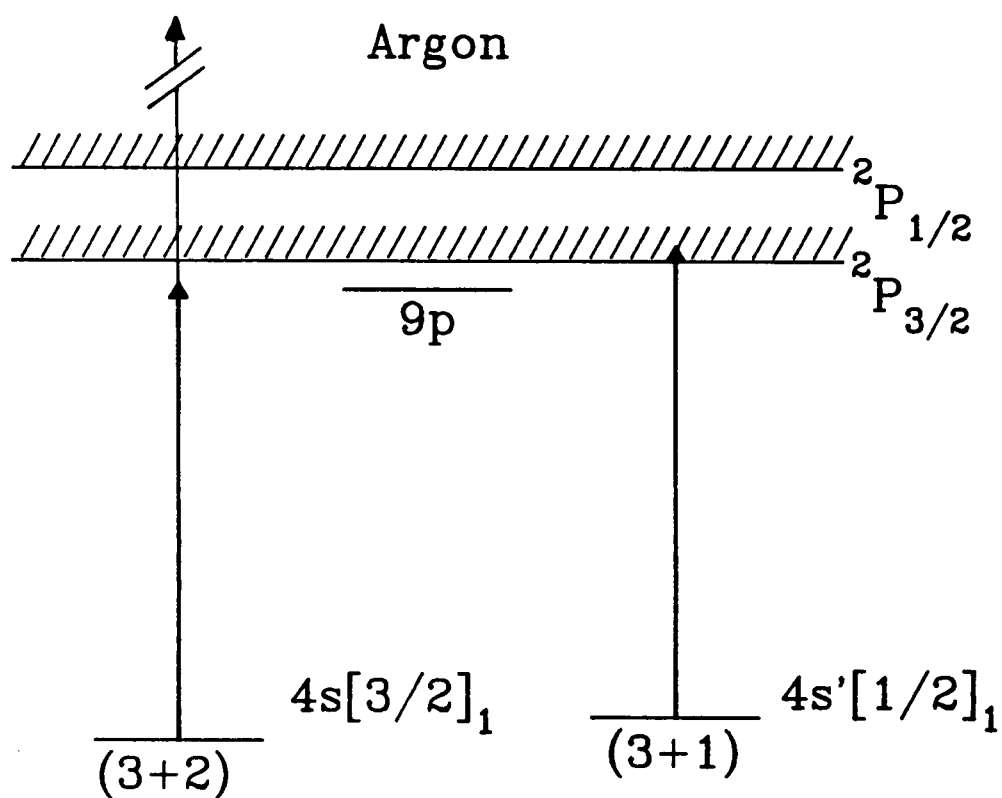


Figure III-4. Potential energy level diagram showing the two- and one- photon ionization from the $4s[3/2]_1$ and $4s'[1/2]_1$ excited states of argon. Note that the absorption of one photon from the $4s[3/2]_1$ lies near the $9p$ manifold.

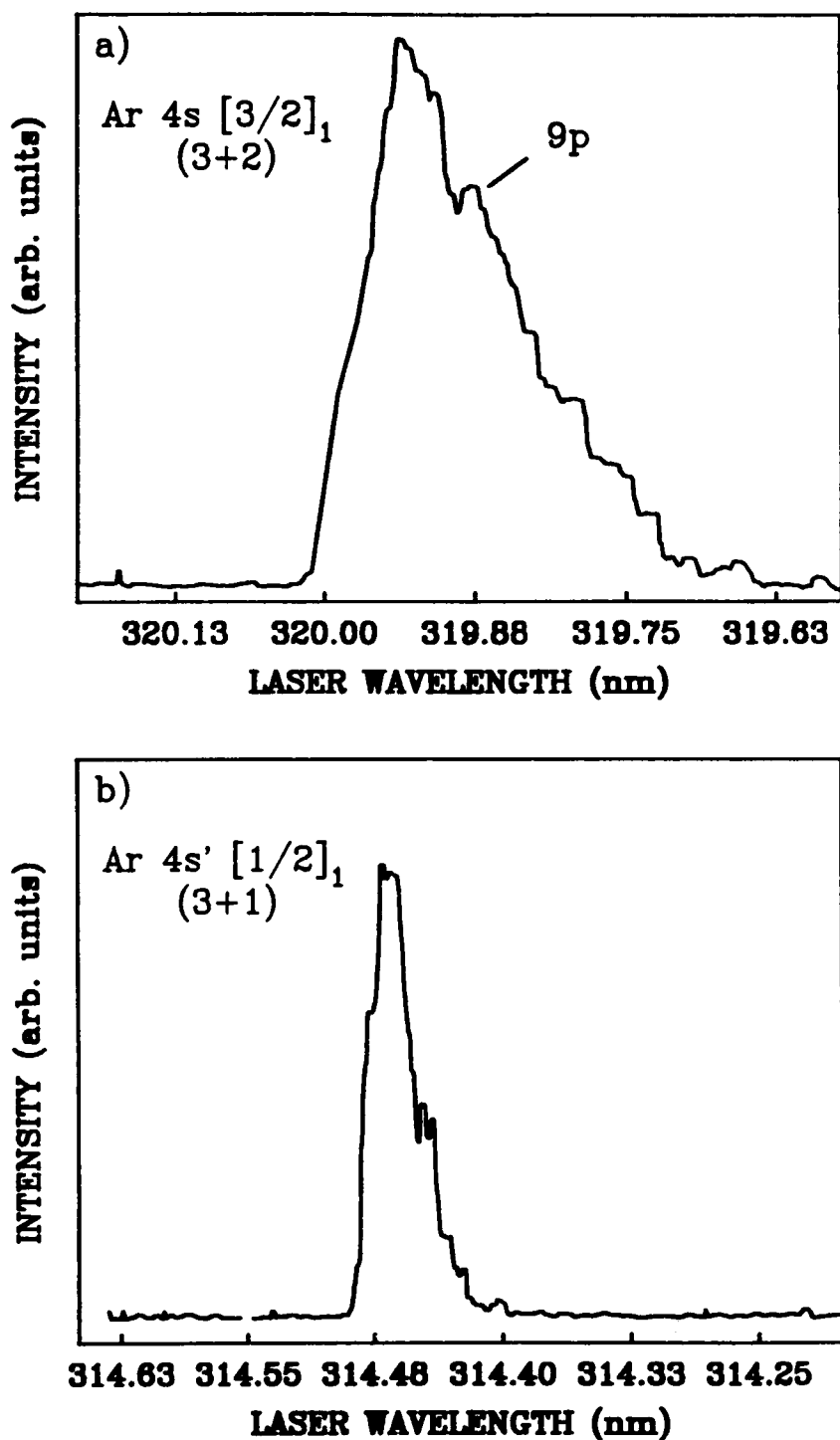


Figure III-5. Resonantly enhanced (3+2) and (3+1) multiphoton ionization via the (a) $4s[3/2]_1$ and (b) $4s'[1/2]_1$ excited states of argon as a function of wavelength. The second peak in (a) corresponds to resonantly enhanced (4+1) multiphoton ionization via the $9p[3/2]_2$ state of argon.

energy of 1 eV. The corrected energy of these photoelectrons was 3.62 eV. This energy corresponds to leaving the ion in the $^2P_{3/2}$ ionic core. Although the fifth photon lies above both thresholds, with a difference in energy of 0.177 eV, there was no evidence of photoelectrons leaving the other ion core as is expected in the j-1 coupling scheme.

Resonantly enhanced (3+1) MPI via the $4s'[1/2]_1$ state also produced only one group of electrons. These electrons were also accelerated into the electrostatic analyzer with an energy of 1 eV. The corrected energy of these photoelectrons was 0.015 eV. The four-photon level lies between the two ionization thresholds. No higher energy electrons were observed in the energy spectrum corresponding to the absorption of a fifth photon (above threshold ionization). Therefore, the observed photoelectrons correspond to leaving the ion in the $^2P_{3/2}$ ionic core. This corresponds to complete core changing during the ionization process. The intensity of the two photoelectron signals were too weak to measure photoelectron angular distributions.

Krypton. Figure III-6 shows the relevant energy levels for three-photon excitation processes studied in krypton. The absorption of an additional photon from these excited levels leads to ionization except for the $5s[3/2]_1$ state

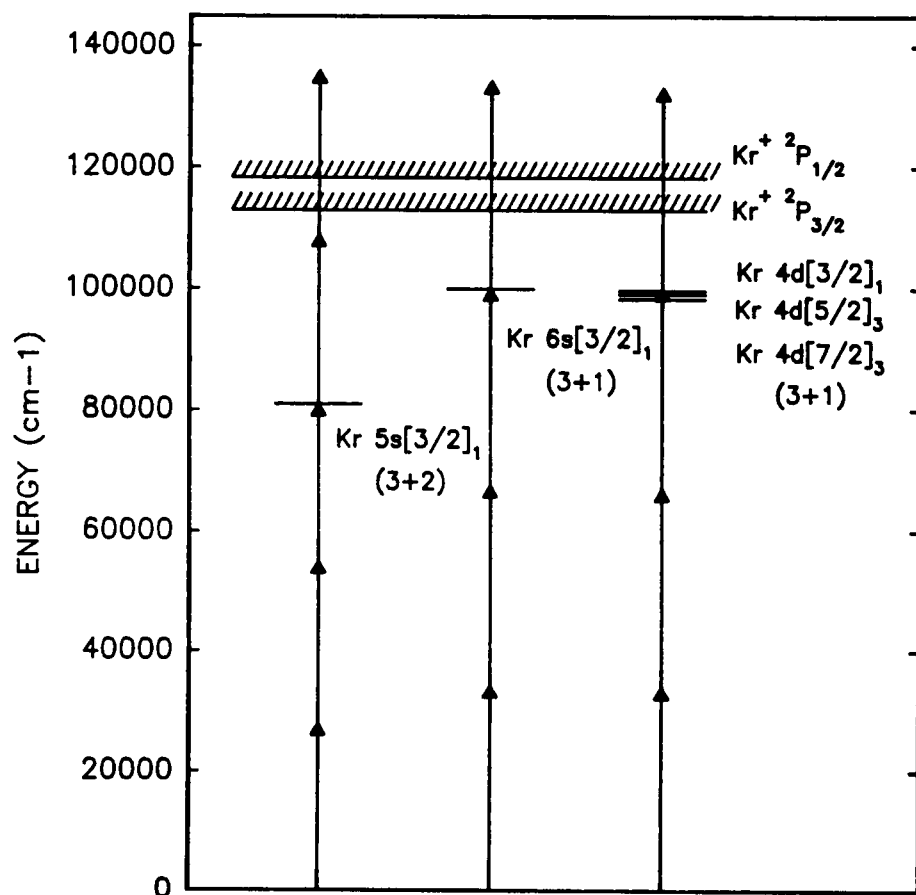


Figure III-6. Potential energy level diagram showing the three photon excitation, four and five-photon ionization processes studied in krypton.

which requires the absorption of two photons for ionization to occur. The energy required for resonantly enhanced multiphoton ionization from these excited levels is sufficient to produce either the $^2P_{1/2}$ or the $^2P_{3/2}$ state of the ion.

The measured energies of the photoejected electrons from resonantly enhanced (3+2) MPI via the $5s[3/2]_1$ state and (3+1) MPI via the $6s[3/2]_1$, $4d[3/2]_1$, $4d[5/2]_3$, and $4d[7/2]_3$ states of krypton are presented in table III-1. Resonantly enhanced MPI through all of the states in table III-1 except for the $6s[3/2]_1$ state yields electrons leaving predominately the $^2P_{3/2}$ ionic core.

The photoelectron energy spectrum resulting from resonantly enhanced (3+1) MPI through the $6s[3/2]_1$ state of krypton is shown in figure III-2. This energy spectrum is typical of those obtained for the rare gases. In j-1 coupling,¹⁵⁷ the $6s[3/2]_1$ state contains the $^2P_{3/2}$ core configuration and only one photoelectron peak is expected in the energy spectrum. However, the photoelectron energy spectrum consists of two peaks, one at 1.85 eV and another at 2.52 eV corresponding to ionization leaving the $^2P_{1/2}$ and $^2P_{3/2}$ cores, respectively. This indicates that there may be some core changing mechanism occurring during the excitation or ionization process. Such non core preserving in multiphoton ionization processes has been the subject of a number of studies^{111,158-160} and will be discussed further in

Table III-1. Measured energies for photoelectrons observed from resonantly enhanced MPI of krypton and the experimental and theoretical ratios, R, of the generalized total cross sections for leaving the $2P_{1/2}$ and $2P_{3/2}$ ion cores.

STATE	LASER	$2P_{1/2}$ (ev)	$2P_{3/2}$ (ev)	$R\left(\frac{2P_{1/2}}{2P_{3/2}}\right)_{EXPT}$	$R\left(\frac{2P_{1/2}}{2P_{3/2}}\right)_{TH}$
WAVELENGTH					
Kr 5s[3/2] ₁ (3+2)	3707Å	-	2.73	<0.01	0.06
Kr 6s[3/2] ₁ (3+1)	3003Å	1.85	2.52	0.36	0.12
Kr 4d[3/2] ₁ (3+1)	3011Å	1.81	2.48	<0.01	0.035
Kr 4d[5/2] ₃ (3+1)	3028Å	1.72	2.39	<0.01	0.022
Kr 4d[7/2] ₃ (3+1)	3054Å	1.58	2.25	<0.01	0.092

the section on xenon.

The experimental ratio, $R(^2P_{1/2}/^2P_{3/2})$, of the integrated photoelectron intensities for leaving the two ion cores is also given in table III-1. This ratio was determined by integrating the intensity of each angular distribution i. e.,

$$\int_0^\pi I(\theta) d\theta, \quad (\text{III-9})$$

and then performing the ratio. Thus, R can be considered as a ratio of the generalized ionization cross sections for leaving the two ion cores. Values of $R < 0.01$ indicate that the $^2P_{1/2}$ ion core was observed in the photoelectron energy spectrum but the signal intensity was too small to measure an angular distribution. The calculated ratio using MQDT is also presented in table III-1. In all cases for krypton there is reasonable agreement between the experimental and calculated ratios.

The measured angular distributions for resonantly enhanced (3+2) MPI via the $5s[3/2]_1$ and the (3+1) MPI via the $6s[3/2]_1$ states of krypton are presented in figure III-7. The solid dots represent the raw data. The solid line represents a Legendre polynomial fit of equation III-5. The dashed line represents the calculated angular distribution from MQDT. The calculated β_{2i} coefficients for a least-squares fit of the experimental data to a Legendre polynomial are presented in table III-2. The β_{2i}

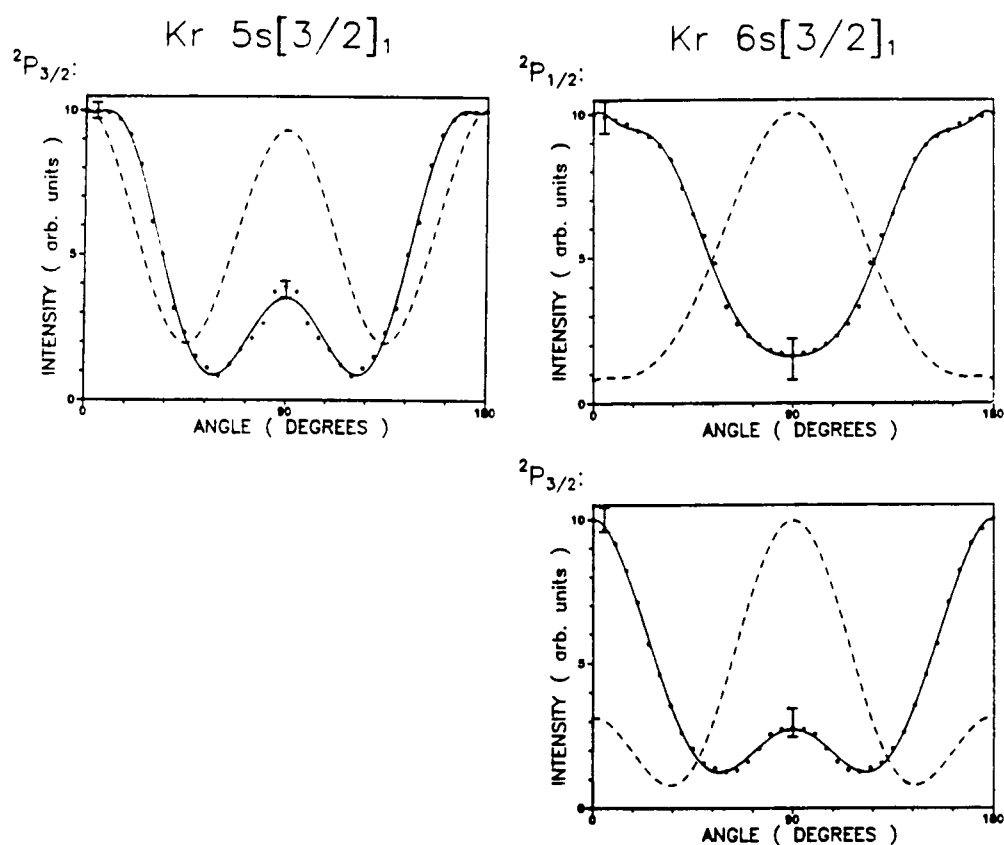


Figure III-7. Photoelectron angular distributions for resonantly enhanced (3+2) MPI via the $5s[3/2]_1$ state of krypton and resonantly enhanced (3+1) MPI via the $6s[3/2]_1$ state of krypton. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-2. The dashed line represents a MQDT generated angular distribution.

Table III-2. β_{2i} coefficients for Legendre polynomial fit of experimental data for three-photon resonantly MPI-PES studies in krypton.

STATE	CORE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$	$\beta(8)$	$\beta(10)$
Kr 5s[3/2] ₁	$2P_{3/2}$	1	1.20	1.579	-0.444	0.047	-0.228
Kr 6s[3/2] ₁	$2P_{1/2}$	1	1.381	0.093	-0.219	0.088	-
Kr 6s[3/2] ₁	$2P_{3/2}$	1	1.081	1.415	1.99E-03	0.124	-
Kr 4d[3/2] ₁	$2P_{3/2}$	1	1.916	0.412	-3.44E-03	-0.034	-
Kr 4d[5/2] ₃	$2P_{3/2}$	1	1.389	0.074	-0.544	0.088	-
Kr 4d[7/2] ₃	$2P_{3/2}$	1	1.580	0.850	0.078	-0.131	-

coefficients obtained from MQDT are presented in table III-3.

The "fourth photon" of the resonantly enhanced (3+2) MPI process via the $5s[3/2]_1$ state lies at 13.127 eV. There are no atomic levels at this energy and therefore no core admixture due to state mixing is expected to occur.

Both of the experimentally measured angular distributions of the photoelectrons leaving the $^2P_{3/2}$ ion core via the resonantly enhanced (3+2) and (3+1) MPI processes via the $5s[3/2]_1$ and $6s[3/2]_1$ states of krypton, respectively, show maxima at 0 and 180° and a small maximum at 90°. The photoelectrons leaving the $^2P_{1/2}$ ion core via resonantly enhanced (3+1) MPI process through the $6s[3/2]_1$ state show a broad distribution with maxima at 0 and 180° with some structure.

The measured photoelectron angular distributions for resonantly enhanced (3+1) MPI via the $4d[3/2]_1$, $4d[5/2]_3$, and $4d[7/2]_3$ states of krypton are presented in figure III-8. The general shapes of these angular distributions are similar except for the $4d[5/2]_3$ state which shows very detailed structure at 0°, 90° and 180°. The experimental and calculated β_{2i} coefficients are presented in tables III-2 and III-3, respectively.

Xenon. The relevant energy levels for the three photon resonant, four photon ionization processes studied in xenon

Table III-3. Calculated β_{2i} coefficients for three-photon resonant processes in krypton.

STATE	CORE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$	$\beta(8)$	$\beta(10)$
Kr 5s[3/2] ₁	$2P_{3/2}$	1	-0.475	1.290	5.89E-03	8.78E-03	1.56E-02
Kr 6s[3/2] ₁	$2P_{1/2}$	1	-1.180	0.320	-3.29E-03	4.32E-03	-
Kr 6s[3/2] ₁	$2P_{3/2}$	1	-1.333	0.954	4.83E-04	0.013	-
Kr 4d[3/2] ₁	$2P_{3/2}$	1	1.670	0.689	7.96E-03	5.57E-03	-
Kr 4d[5/2] ₃	$2P_{3/2}$	1	1.283	0.678	-6.69E-02	9.66E-03	-
Kr 4d[7/2] ₃	$2P_{3/2}$	1	1.189	0.586	-0.432	1.12E-02	-

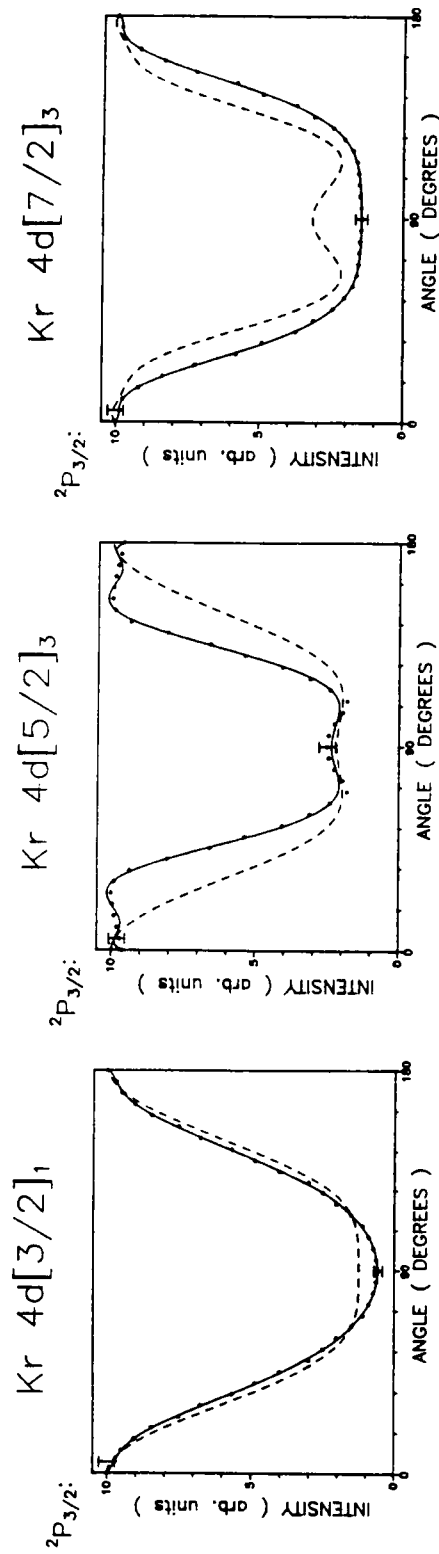


Figure III-8. Photoelectron angular distributions for resonantly enhanced (3+1) MPI via the $4d[3/2]_1$, $4d[5/2]_3$, and $4d[7/2]_3$ states of krypton. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-2. The dashed line represents a MQDT generated angular distribution.

are shown in figure III-9. MPI through these levels leads to one or two photoelectron peaks allowing assignment to either the $^2P_{1/2}$ or the $^2P_{3/2}$ ion core. The measured energies of the photoelectrons from resonantly enhanced (3+1) MPI of the $7s[3/2]_1$, $8s[3/2]_1$, $9s[3/2]_1$, $5d[3/2]_1$, $5d'[5/2]_3$, $5d'[3/2]_1$ states of xenon are presented in table III-4 along with the measured and calculated ratios, R , of the integrated intensities for leaving both ion cores.

Interestingly, energy analysis of the photoelectrons show that resonantly enhanced MPI through the $5d[3/2]_1$ state yields only $^2P_{3/2}$ ion core and resonantly enhanced MPI through the $5d'[5/2]_3$ and $5d'[3/2]_1$ states yield only the $^2P_{1/2}$ ion core, exhibiting complete core preservation as is expected in $j-1$ coupling. Resonantly enhanced MPI through the $7s[3/2]_1$, $8s[3/2]_1$ and $9s[3/2]_1$ states yield photoelectrons from both ion cores.

Since, in the $j-1$ coupling scheme,¹⁵⁷ the $7s[3/2]_1$, $8s[3/2]_1$ and $9s[3/2]_1$ states of xenon have a $^2P_{3/2}$ core configuration, only one photoelectron peak is expected corresponding to leaving the ion in its parent core. This type of core changing during ionization has previously been observed and analyzed for the $6s[3/2]_1$ state of xenon at low laser intensities.^{111,158} Usually, core changing has been attributed to accidental resonances with autoionizing or doubly excited states above the atom's lowest ionization threshold.¹⁶¹⁻¹⁶³ In a recent study by Blazewicz et al.¹⁶⁰ it

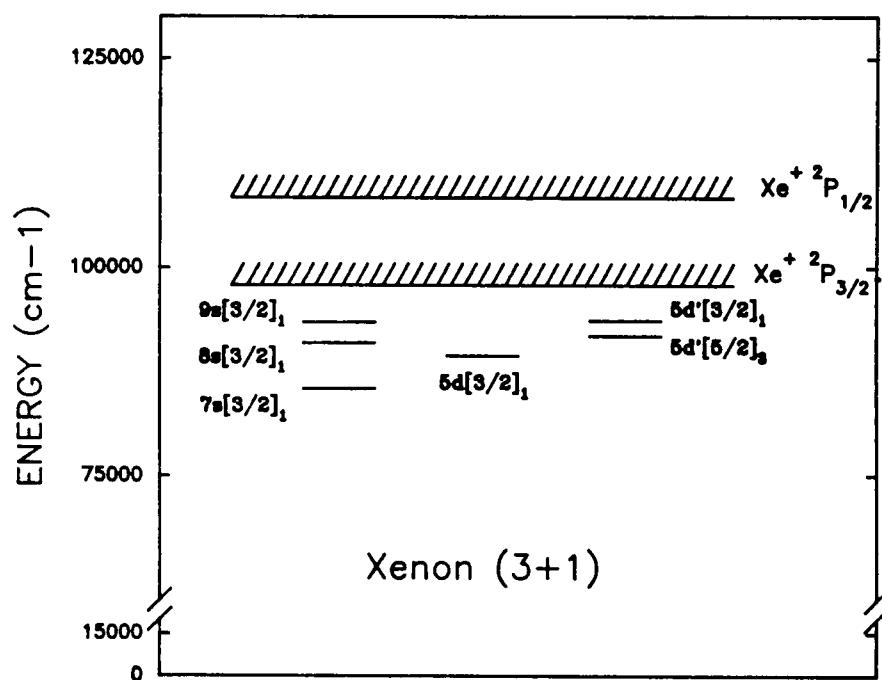


Figure III-9. Potential energy level diagram showing the three-photon excitation, four-photon ionization processes studied in xenon.

Table III-4. Measured energies for photoelectrons observed from resonantly enhanced MPI of xenon and the experimental and theoretical ratios, R , of the generalized cross sections for leaving the $2P_{1/2}$ and $2P_{3/2}$ ion cores.

STATE	LASER	$2P_{1/2}$ (eV)	$2P_{3/2}$ (eV)	$R\left(\frac{2P_{1/2}}{2P_{3/2}}\right)_{EXPT}$	$R\left(\frac{2P_{1/2}}{2P_{3/2}}\right)_{TH}$
WAVELENGTH					
Xe 7s[3/2] ₁ (3+1)	3511Å	0.68	1.99	0.54	0.21
Xe 8s[3/2] ₁ (3+1)	3299Å	1.59	2.90	1.31	0.73
Xe 9s[3/2] ₁ (3+1)	3211Å	2.00	3.31	8.00	0.8
Xe 5d[3/2] ₁ (3+1)	3576Å	-	1.74	0	0.097
Xe 5d'[5/2] ₃ (3+1)	3270Å	1.73	-	>10	-
Xe 5d'[3/2] ₁ (3+1)	3204Å	2.04	3.35	>10	4.1
Xe 6p[1/2] ₀ (2+1)	2486Å	1.46	2.77	0.29	0.16
Xe 6p[3/2] ₂ (2+1)	2525Å	-	2.60	0	0.09
Xe 6p'[1/2] ₀ (2+1)	2226Å	3.27	4.58	>10	4.53
Xe 6p'[3/2] ₂ (2+1)	2243Å	3.14	-	>10	9.35
Xe 7p[1/2] ₀ (2+1)	2251Å	3.08	4.39	0.98	1.04
Xe 7p[3/2] ₂ (2+1)	2255Å	3.05	4.36	0.42	0.44
Xe 7p[5/2] ₂ (2+1)	2264Å	3.01	4.32	0.28	0.38

was found that the $6s[3/2]_1$ state in xenon had substantial 5d character. Mixing of the 5d and 6s states is not expected to produce any core admixture since both states contain the $^2P_{3/2}$ core configuration. However, this state mixing allows for enhancement with 4f levels which lie at the four photon level in this resonantly enhanced (3+2) MPI process. The 4f levels themselves would not induce any core admixture since they too contain the $^2P_{3/2}$ core configuration. However the observed MPI signal is strongly ac Stark broadened due to strong coupling with the $6p'$ manifold. Hence, core admixture is introduced at the four photon level. Perry and Landen¹⁶⁴ observed that the branching ratios of the photoelectrons in krypton and xenon were dependent upon the intensity of the laser ($I \sim 3 \times 10^{12}$ to 10^{14} W/cm²). The ratios were explained quantitatively by the influence of intermediate states being shifted into resonance by the presence of the intense laser field.

Absorption of an additional photon from the $7s[3/2]_1$, $8s[3/2]_1$, and $9s[3/2]_1$ levels leads to ionization in the open continuum, hence no core admixture due to state coupling is introduced at the fourth photon level in this study. No autoionizing or doubly excited states are present at the four-photon level either. At the laser intensities employed in this study ($I < 10^{11}$ W/cm²), no ac stark shifting of levels into resonance is expected. The observation of photoelectrons leaving both ion cores is interpreted as

evidence that the $7s[3/2]_1$, $8s[3/2]_1$ and $9s[3/2]_1$ states may not be pure $^2P_{3/2}$ configurations. For $J=1$ odd parity states, descriptive wave functions include three channels, $5p^6(^2P_{3/2})ns[3/2]$, $5p^6(^2P_{3/2})nd[1/2]$, $5p^6(^2P_{3/2})nd[3/2]$, converging to the first ionization threshold and two channels, $5p^6(^2P_{3/2})ns'[1/2]$, $5p^6(^2P_{3/2})nd'[3/2]$, converging to the second ionization threshold.¹⁵⁴ An MQDT calculation indicates that the mixing coefficients of the five channels for the $7s[3/2]_1$, $8s[3/2]_1$ and $9s[3/2]_1$ states are non-zero. The extent of this admixture is represented by the ratio, R . Comparison between the experimental and calculated ratios, R , demonstrate that the wave functions used in the MQDT adequately describe the resonant intermediate states of krypton and xenon.

The angular distributions of the photoemitted electrons from the $7s[3/2]_1$, $8s[3/2]_1$ and $9s[3/2]_1$ states of xenon are shown in figure III-10. The photoelectrons resulting in leaving the $^2P_{1/2}$ ion core, in general, show a broad distribution with maxima at 0° and 180° with the distribution from the $7s$ state showing a more complex distribution. The photoemitted electrons leaving the $^2P_{3/2}$ ion core by far show the most interesting distributions. The $7s$ state shows a somewhat isotropic distribution with a maxima at 90° and minima at 0° and 180° . The $8s$ state also shows a somewhat isotropic distribution with two maxima at 45° and 135° and minima at 0° , 90° and 180° . The $9s$ state

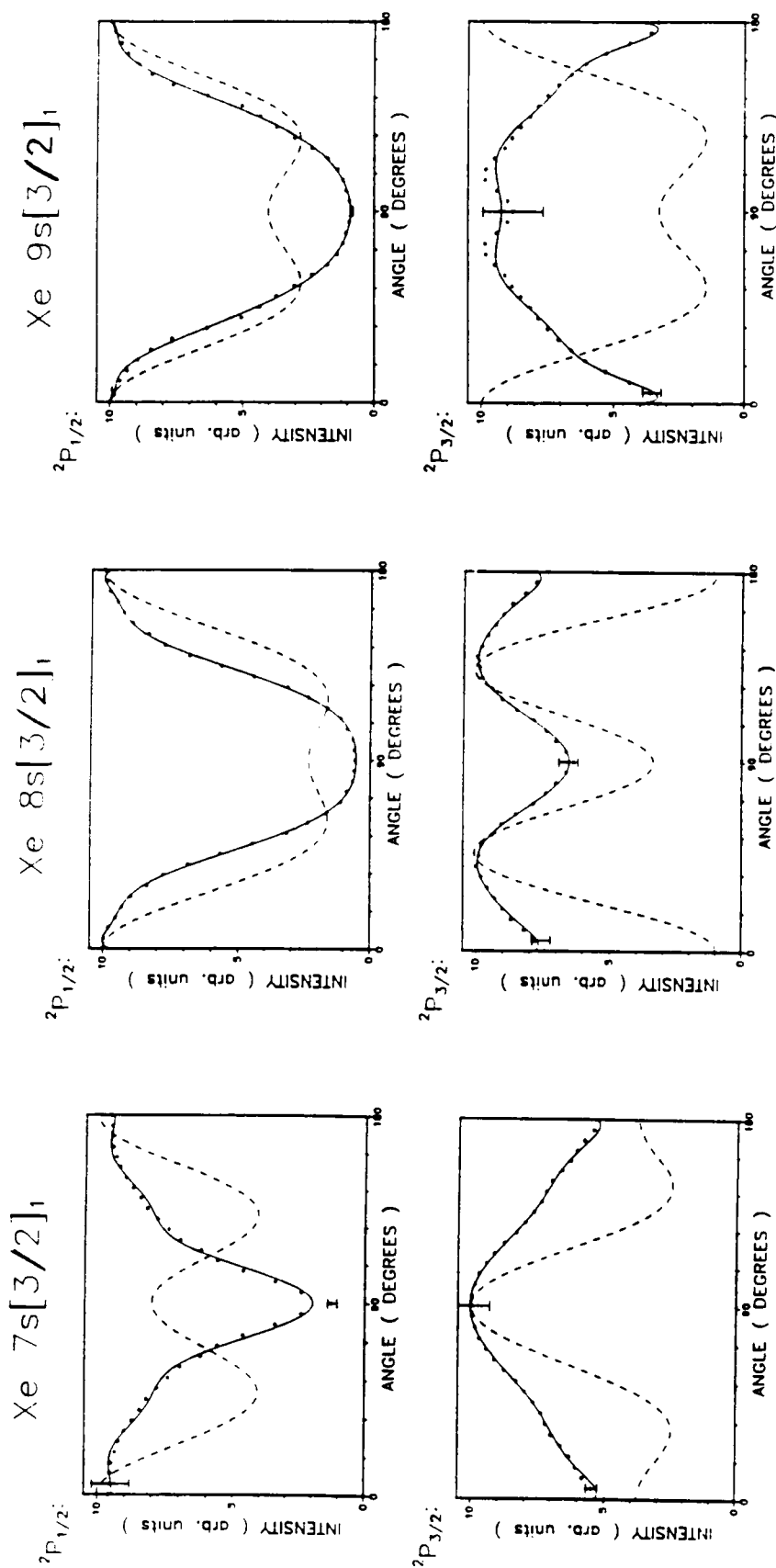


Figure III-10. Photoelectron angular distributions for resonantly enhanced (3+1) MPI via the $7s[3/2]_1$, $8s[3/2]_1$, and $9s[3/2]_1$ states of xenon. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-5. The dashed line represents a MQDT generated angular distribution.

shows an even more isotropic distribution with a double maxima at 80° and 100° and minima at 0° and 180° . Since photoelectron angular distributions involve the addition of all the amplitudes of transitions leading to different final states, the complexity of the $^2P_{3/2}$ photoelectron angular distribution arises from the strong channel couplings, as indicated by the ratio R , of the outgoing waves. The β_{2i} coefficients for a least-squares fit of the experimental data are presented in table III-5. The β_{2i} coefficients obtained by MQDT are presented in table III-6.

The measured and calculated photoelectron angular distributions for resonantly enhanced (3+1) MPI via the $5d[3/2]_1$, $5d'[3/2]_1$, and $5d'[3/2]_1$ states of xenon are shown in figure III-11. The β_{2i} coefficients for a least-squares fit of the experimental data and those obtained by MQDT are presented in tables III-5 and III-6, respectively.

The measured energies of photoelectrons from resonantly enhanced (2+1) MPI of the $6p[1/2]_0$, $6p[3/2]_2$, $6p'[1/2]_0$, $6p'[3/2]_2$, $7p[1/2]_0$, $7p[3/2]_2$, and $7p[5/2]_2$ states of xenon are presented in table III-4. Photoelectrons from both the $^2P_{1/2}$ and the $^2P_{3/2}$ ion cores are observed for these (2+1) MPI processes except for the $6p[3/2]_2$ and $6p'[3/2]_2$ states which yield predominately photoelectrons from the $^2P_{1/2}$ and $^2P_{3/2}$ ion core, respectively. Comparison of the integrated intensity ratio, R , shows excellent agreement between experiment and theory. The angular distributions for ionization through

Table III-5. β_{2i} coefficients for Legendre polynomial fit of experimental data for three-photon resonantly enhanced MPI-PES studies in xenon.

STATE	CORE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$	$\beta(8)$
Xe 7s[3/2]1	$2P_{1/2}$	1	0.785	-0.424	0.299	-0.160
Xe 7s[3/2]1	$2P_{3/2}$	1	-0.330	0.025	-0.033	-0.044
Xe 8s[3/2]1	$2P_{1/2}$	1	1.925	0.028	-0.322	0.087
Xe 8s[3/2]1	$2P_{3/2}$	1	0.227	-0.298	0.012	-0.037
Xe 9s[3/2]1	$2P_{1/2}$	1	1.755	0.321	-0.080	-0.103
Xe 9s[3/2]1	$2P_{3/2}$	1	-0.309	-0.157	7.44E-03	-0.140
Xe 5d[3/2]1	$2P_{3/2}$	1	1.351	0.751	0.1981	-0.066
Xe 5d'[3/2]1	$2P_{1/2}$	1	2.341	1.126	-0.018	0.069
Xe 5d'[5/2]3	$2P_{1/2}$	1	1.422	0.912	0.508	-0.180

Table III-6. Calculated β_{2i} coefficients for three-photon resonant processes in xenon.

STATE	CORE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$	$\beta(8)$
Xe 7s[3/2]1	$2p_{1/2}$	1	-0.083	0.740	-1.05E-02	6.480E-03
Xe 7s[3/2]1	$2p_{3/2}$	1	-0.942	0.555	2.33E-02	-4.501E-02
Xe 8s[3/2]1	$2p_{1/2}$	1	1.230	1.082	8.48E-03	0.007
Xe 8s[3/2]1	$2p_{3/2}$	1	0.231	-1.055	-2.83E-02	-0.1225E-2
Xe 9s[3/2]1	$2p_{1/2}$	1	0.601	0.816	3.51E-02	2.826E-03
Xe 9s[3/2]1	$2p_{3/2}$	1	0.823	1.371	0.081	9.723E-03
Xe 5d[3/2]1	$2p_{3/2}$	1	1.400	0.613	1.72E-02	-6.855E-03
Xe 5d'[3/2]1	$2p_{1/2}$	1	1.324	0.712	-8.49E-04	1.265E-02
Xe 5d'[5/2]3	$2p_{1/2}$	1	1.422	0.912	0.508	-0.180

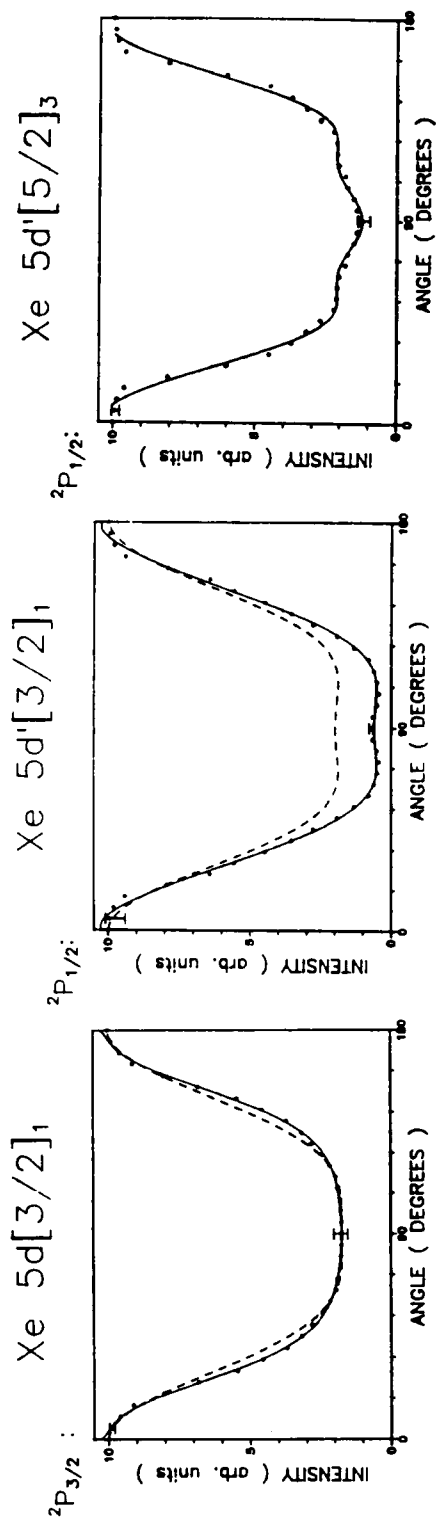


Figure III-11. Photoelectron angular distributions for resonantly enhanced (3+1) MPI via the 5d[3/2]₁, 5d'[3/2]₁, and 5d'[5/2]₃ states of xenon. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-5. The dashed line represents a MQDT generated angular distribution.

the $6p[1/2]_0$ and $6p[3/2]_2$ states are shown in figure III-12. The measured and calculated angular distributions for resonantly enhanced (2+1) MPI via the $6p'[3/2]_2$ state are shown in figure III-13. A distinct power dependence was observed for the angular distribution of the photoemitted electrons that result from leaving the $2p_{1/2}$ ionic core via the resonantly enhanced (2+1) MPI of the $6p'[1/2]_0$ excited state. At high laser power ($3.2 \times 10^{10} \text{ W/cm}^2$) the general shape is approximately $A + B\cos^2\theta$, as predicted by MQDT. At lower laser powers ($1.6 \times 10^{10} \text{ W/cm}^2$) some structure is observed at 90° which we cannot explain at this time. The measured angular distribution at two different laser powers along with the MQDT generated angular distribution is shown in figure III-14. It is rather doubtful that this observed power dependence is brought on as a result of an ac Stark contribution of other levels at this power density since the nearest two-photon allowed state is 708cm^{-1} below the $6p'[1/2]_0$ state.

One possibility could involve the generation of third harmonic light at high power which would yield a $A + B\cos^2\theta$ distribution of photoelectrons. At lower power, the multiphoton ionization process would dominate over the one-photon ionization process, involving third harmonic light, yielding the observed angular distribution. Such a power dependence was not observed for resonantly enhanced MPI via other states studied in the same power range.

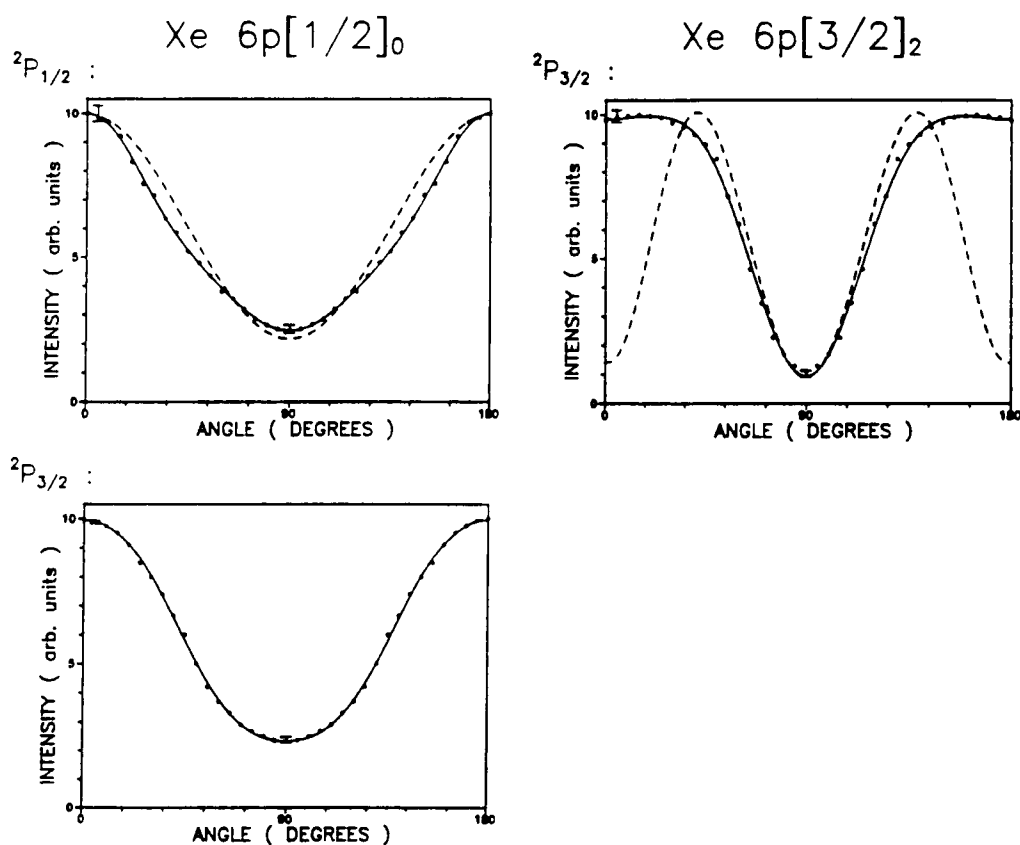


Figure III-12. Photoelectron angular distributions for resonantly enhanced (2+1) MPI via the $6p[1/2]_0$, $6p[3/2]_2$, states of xenon. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-7. The dashed line represents a MQDT generated angular distribution.

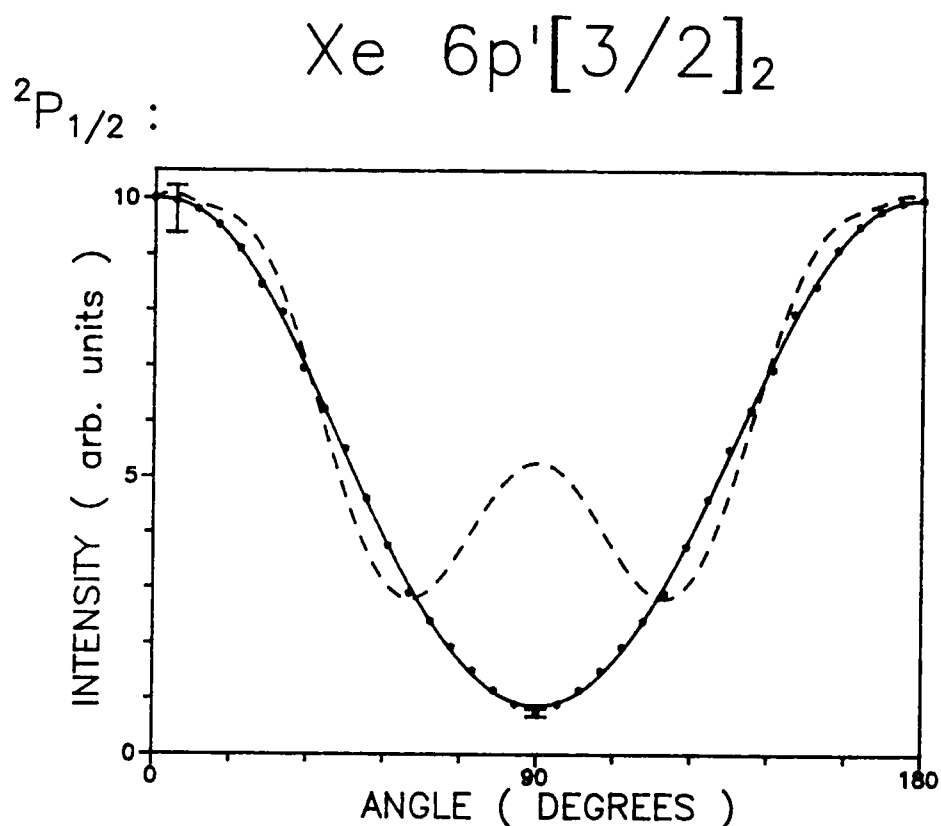


Figure III-13. Photoelectron angular distributions for resonantly enhanced (2+1) MPI via the $6p'[3/2]_2$ state of xenon. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-7. The dashed line represents a MQDT generated angular distribution.

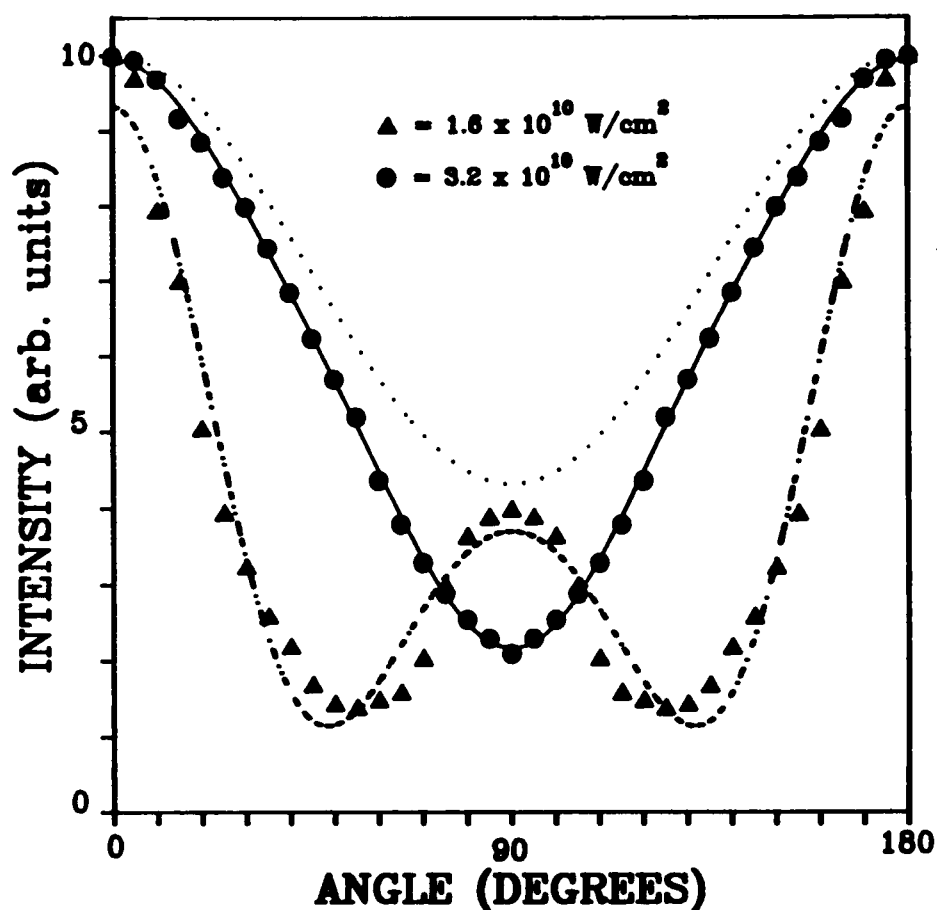


Figure III-14. Photoelectron angular distribution for resonantly enhanced (2+1) MPI via the $6p'[1/2]$ state of xenon at two different laser powers. The solid triangles (▲) correspond to a laser power of $1.6 \times 10^{10} \text{ W/cm}^2$. The solid circles (●) correspond to a laser power of $3.2 \times 10^{10} \text{ W/cm}^2$. The dashed line represents a MQDT generated angular distribution. This type of power dependence was not observed in any of the other measured photoelectron angular distributions in the same power range.

The angular distributions for resonantly enhanced (2+1) MPI via the $7p[1/2]_0$, $7p[3/2]_2$, and $7p[5/2]_2$ states are shown in figure III-15. The measured and calculated β_{2i} coefficients are presented in tables III-7 and III-8, respectively.

Comparison of the measured and calculated angular distributions shows that there is reasonable agreement between experiment and theory in describing the general shape of the angular distribution except for the $6s[3/2]_1$ state of krypton and the $9s[3/2]_1$ state of xenon. It is interesting to note that comparison of the ratio of the integrated photoelectron intensities between experiment and theory for the $9s[3/2]_1$ state also do not agree. MQDT takes into account various intrachannel and interchannel interactions between different Rydberg series and provides an accurate description of the atomic spectrum and wave functions. The semi-empirical approach, which is based on fitting the experimental data, is less accurate in describing the ground state and perhaps some of the low lying excited states which are often excluded from the fitting procedure.¹⁶⁵

The lack of detail (structure), as predicted by MQDT, in the experimental angular distribution can perhaps be explained by hyperfine coupling effects which are known in the case of some alkali atoms to partially destroy the anisotropy produced in the excitation process.¹³²⁻¹³⁵

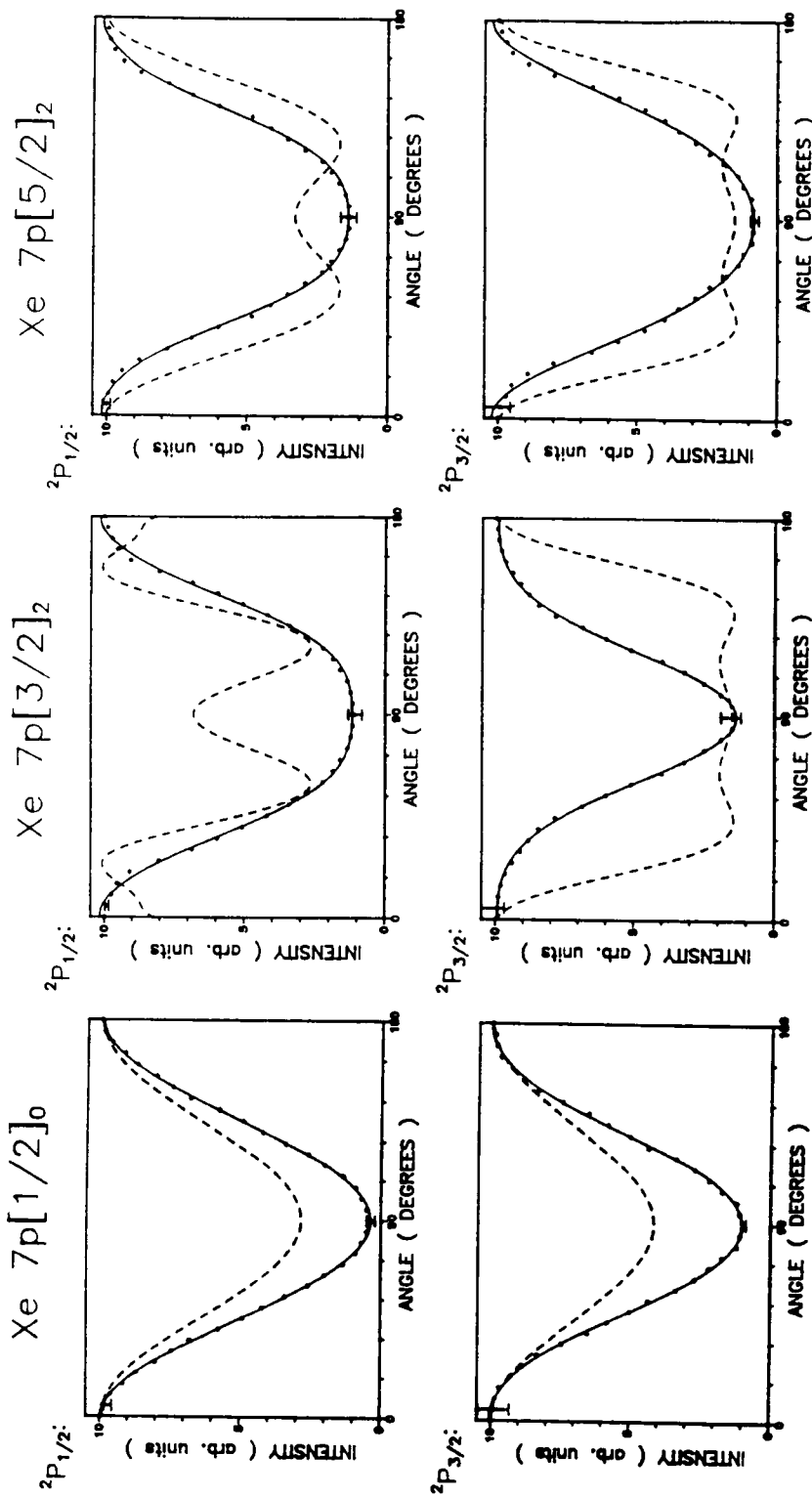


Figure III-15. Photoelectron angular distributions for resonantly enhanced (2+1) MPI via the $7p[1/2]_0$, $7p[3/2]_2$, and $7p[5/2]_2$ states of xenon. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-7. The dashed line represents a MQDT generated angular distribution.

Table III-7. β_{2i} coefficients for Legendre polynomial fit of experimental data from two-photon resonant processes in xenon.

STATE	CORE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$
Xe 6p[1/2] ₀	² P _{1/2}	1	0.965	0.154	0.111
Xe 6p[1/2] ₀	² P _{3/2}	1	1.116	9.97E-02	-7.46E-02
Xe 6p[3/2] ₂	² P _{3/2}	1	1.198	-0.5814	0.085
Xe 6p'[1/2] ₀	² P _{1/2} (a)	1	0.386	1.548	0.314
Xe 6p'[1/2] ₀	² P _{1/2} (b)	1	1.028	-0.068	0.064
Xe 6p'[3/2] ₂	² P _{1/2}	1	1.599	0.025	-0.040
Xe 7p[1/2] ₀	² P _{1/2}	1	1.821	0.047	4.12E-03
Xe 7p[1/2] ₀	² P _{3/2}	1	1.503	-0.055	-0.048
Xe 7p[3/2] ₂	² P _{1/2}	1	1.666	0.422	-0.077
Xe 7p[3/2] ₂	² P _{3/2}	1	1.207	-0.357	0.023
Xe 7p[5/2] ₂	² P _{1/2}	1	1.512	0.210	-0.128
Xe 7p[5/2] ₂	² P _{3/2}	1	1.748	0.372	0.032

a = high laser power
b = low laser power

Table III-8. Calculated β_{2i} coefficients for two photon resonant processes in xenon.

STATE	CORE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$
Xe 6p[1/2] ₀	² P _{1/2}	1	1.093	5.69E-03	5.37E-04
Xe 6p[1/2] ₀	² P _{3/2}	1	-	-	-
Xe 6p[3/2] ₂	² P _{3/2}	1	0.776	-1.359	-0.193
Xe 6p'[1/2] ₀	² P _{1/2}	1	0.609	9.30E-03	2.58E-03
Xe 6p'[3/2] ₂	² P _{1/2}	1	0.713	0.735	-0.464
Xe 7p[1/2] ₀	² P _{1/2}	1	0.915	-3.74E-03	4.51E-04
Xe 7p[1/2] ₀	² P _{3/2}	1	0.638	-1.30E-03	3.94E-04
Xe 7p[3/2] ₂	² P _{1/2}	1	0.565	0.741	-0.807
Xe 7p[3/2] ₂	² P _{3/2}	1	1.025	1.248	1.082
Xe 7p[5/2] ₂	² P _{1/2}	1	0.893	1.182	-3.16E-02
Xe 7p[5/2] ₂	² P _{3/2}	1	-	-	-

Initially, a coherent superposition of hyperfine levels is excited. If the hyperfine precession period is of the same order or shorter than the duration of the ionization pulse, then the anisotropy of the excited state can be partially destroyed due to m_j -mixing resulting from hyperfine coupling of orbital and nuclear spin angular momentum. Xenon has two isotopes which have a nuclear spin other than zero. These two isotopes ($_{54}\text{Xe}^{131}$ ($I=3/2$) and $_{54}\text{Xe}^{129}$ ($I=1/2$)) account for ~48% of the isotope abundance. Table III-9 presents the calculated precession period for several excited states of $_{54}\text{Xe}^{131}$ and shows that the precession periods ($\leq 1\text{ns}$) are significantly shorter than the laser pulse length ($\sim 8\text{ns}$). Hence, hyperfine coupling effects are expected to play a contributing role in the measured photoelectron angular distributions for xenon. The hyperfine parameters for krypton (also shown in table III-9) are approximately the same order of magnitude as that for xenon. The precession periods of krypton are roughly the same as for xenon. Krypton also has two isotopes with a nuclear spin other than zero. However they only account for ~28% of the total isotope abundance and consequently are expected to have a smaller influence on the measured angular distribution.

To examine the extent of hyperfine coupling it would be interesting to compare the angular distribution of an isotopic sample of xenon with pure $I=0$ to the above distributions. However, obtaining such a mixture probably

Table III-9. Hyperfine constants (A and B) and calculated hyperfine precession periods of some selected states in krypton ($I=9/2$) and xenon ($I=3/2$).

STATE	A (MHz)	B (MHz)	hfs period (nS)
Xe 7p[3/2] ₂	278.1 ^b	12 ^a	0.48
Xe 7p[5/2] ₂	395.4 ^b	237 ^a	0.36
Xe 6p[3/2] ₂	263.1 ^d	29 ^d	0.51
Xe 6p'[1/2] ₂	856.1 ^b	-45 ^a	0.16
Xe 6s[3/2] ₁	288 ^b	87 ^b	0.93
Xe 6s'[1/2] ₁	1711 ^c	33 ^c	0.15
Kr 5p'[3/2] ₁	226.8 ^e	22 ^e	0.33
Kr 5p'[3/2] ₂	-291 ^e	30 ^e	0.09
Kr 5p[5/2] ₂	-156 ^e	-410 ^e	0.16

a = S. Liberman, J. Physique 32, 867 (1971)

b = D. A. Jackson et. al., Proc. R. Soc. Lond., A327, 137 (1972)

c = W. Fisher et. al., Z. Physik, 270, 113 (1974)

d = W. Borchers et. al., Phys. Lett., B216, 7 (1989)

e = J. R. Brandenberger, Phys. Rev. A39, 64 (1989).

would be a costly endeavor. Therefore, an alternative method would be to conduct an ion-photoelectron coincidence study in which the angular distribution of photoelectrons would be correlated to the respective isotope.

Interestingly, the isotopes of argon all have a nuclear spin of zero. Argon would be an ideal case to study, since no hyperfine coupling effects would be observed. As discussed earlier, experiments on resonantly enhanced (3+2) MPI via the $4s[3/2]_1$ state and resonantly enhanced (3+1) MPI via the $4s'[1/2]_1$ state of argon were attempted but signals were too low to measure photoelectron angular distributions.

An additional point to consider, which has not been included in this study or in previous studies of the rare gases, is the influence of spin-orbit (relativistic effects) coupling in the continuum. Relativistic effects have recently been observed in cesium,¹⁰⁴ and may need to be included here. Such an analysis is beyond the scope of this thesis.

The measured angular distributions for resonantly enhanced MPI via the four-photon allowed $6p[1/2]_0$ and $6p[3/2]_2$ states of xenon are shown in figure III-16. The measured energies and β_{2i} coefficients for Legendre polynomial fits of these four-photon processes are reported in tables III-10 and III-11, respectively. The fifth photon in both cases lies just above the first ionization threshold ($\text{Xe}^+ 2p_{3/2}$) but not near any autoionizing levels. Therefore,

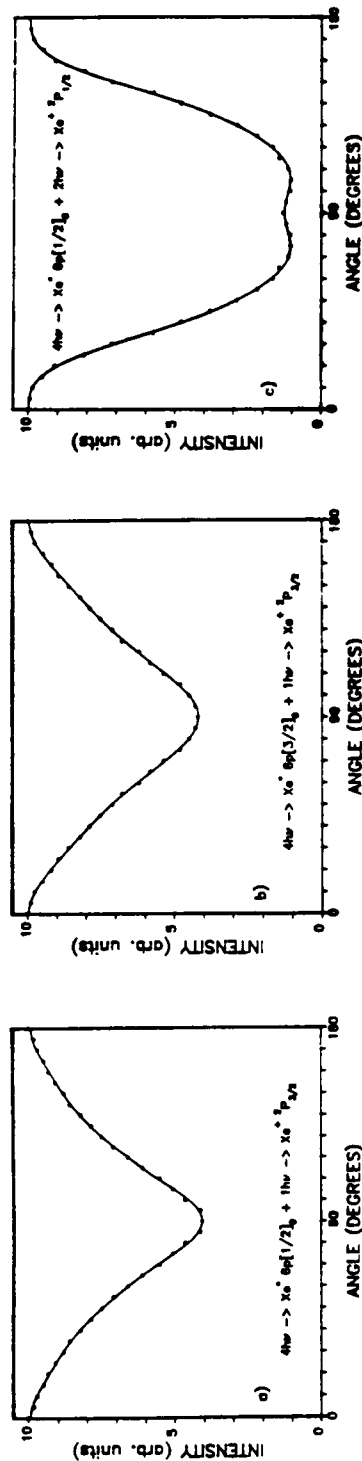


Figure III-16. Experimentally measured photoelectron angular distributions for the four-photon resonant processes studied in xenon. a) and b) show the measured angular distributions for photoelectrons resulting from resonantly enhanced (4+1) MPI via the $6p[1/2]_0$ and $6p[3/2]_2$ states of xenon, respectively. c) shows the measured photoelectron angular distribution due to above threshold ionization from resonantly enhanced (4+1+1) MPI via the $6p[1/2]_0$ state of xenon. The dots (*) represent experimental data points. The solid line (—) represents a Legendre polynomial fit to the experimental data. The β_{2i} coefficients for the fit can be found in table III-11.

Table III-10. Measured energies for four photon processes in xenon.

STATE	CORE	MEASURED ENERGIES (ev)
$6p[3/2]_2 [4+1]$	$^2P_{3/2}$	0.15
$6p[1/2]_0 [4+1]$	$^2P_{3/2}$	0.28
$6p[1/2]_0 [4+2]$	$^2P_{1/2}$	1.46

Table III-11. β_{2i} coefficients for Legendre polynomial fit to experimental data from four-photon resonant processes in xenon.

STATE	CORE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$	$\beta(8)$	$\beta(10)$	$\beta(12)$
$6p[3/2]_2 [4+1]$	$2P_{3/2}$	1	0.577	-0.156	$8.19E-02$	$-2.52E-02$	$2.11E-02$	-
$6p[1/2]_0 [4+1]$	$2P_{3/2}$	1	0.579	-0.092	0.067	$-3.40E-03$	$2.53E-03$	-
$6p[1/2]_0 [4+2]$	$2P_{1/2}$	1	1.838	0.663	-0.179	-0.050	-0.103	$8.44E-03$

only one photoelectron peak is expected in the photoelectron energy spectrum as in the case of (4+1) photoionization from the $6p[3/2]_2$ state. However, a second peak is observed in the photoelectron energy spectrum of the $6p[1/2]_0$ state corresponding to absorption of an additional photon leading to "above threshold ionization" (figure III-17). This results in photoelectrons leaving the $^2P_{1/2}$ ionic core. This additional peak was only observed when the laser was tuned to resonance with the $6p[1/2]_0$ state. The measured angular distribution for above threshold ionization is shown in figure III-16c. It is interesting to note that it shows a subsidiary peak structure at 90° . No MQDT generated distribution is presently available. Electron signals due to 7 or 8 photon absorption above threshold ionization were not detected.

Comparison of the photoelectron angular distributions via the resonantly enhanced (4+1) MPI processes with that of the resonantly enhanced (2+1) MPI processes from the same excited states show that the general shapes of the angular distributions are identical except at 90° where the signal intensity is greater in the resonantly enhanced (4+1) MPI process than in the resonantly enhanced (2+1) MPI process. This can be accounted for by the fact that, although ionization occurs from the same excited state, the energy and angular momentum of the resulting continuum states for the two resonantly enhanced MPI processes are different.

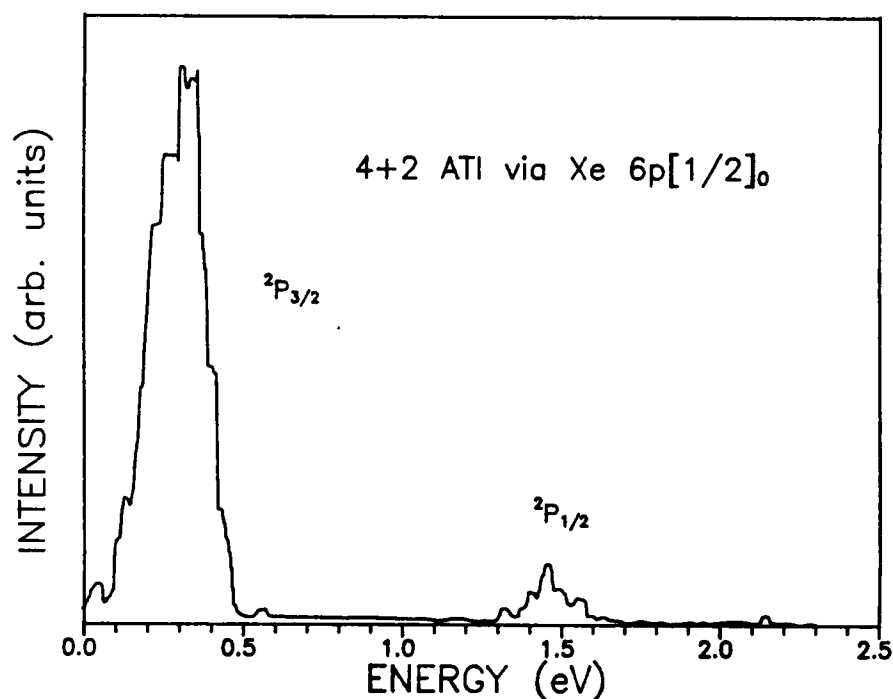


Figure III-17. Above threshold ionization (4+1+1) (photoemitted electrons which result from leaving the $^2P_{1/2}$ ion core) is observed in the photoelectron energy spectrum for the four-photon allowed resonantly enhanced MPI process via the $6p[1/2]_0$ state of xenon yielding ~ 1.5 eV electrons. The photoemitted electrons at ~ 0.3 eV are due to resonantly enhanced MPI which results in leaving the $^2P_{1/2}$ core of the Xe^+ ion.

Molecules

An brief study of resonantly enhanced MPI-PES of various excited electronic states of two hydrocarbons (ethylene and trans-1,3-butadiene) was carried out in a pulsed supersonic nozzle beam with the apparatus described earlier (pg. 49). The results are compared with similar studies done in an MPI cell. The only modification to the beam apparatus was the addition of a double reflectron mass spectrometer to increase mass resolution. The photoelectron energy spectra consisted of a distribution of photoelectron energies corresponding to the vibrational energy of the nascent ion.

A schematic diagram of the double reflectron time-of-flight mass spectrometer is shown in figure III-18. The double reflectron mass spectrometer is based on the original concept of a mass reflectron of Mamyrin et al.¹⁶⁶ The basic components consist of an ion extractor, two ion reflectors, three flight tubes, and a dual micro-channel plate assembly. A series of articles have addressed the design considerations for various components of the reflectron.¹⁶⁷⁻¹⁷⁰

Ions are first extracted from the ionization region at some voltage V_1 and then accelerated to some energy, V_2 . The ions drift in a flight tube kept at V_2 where they separate depending on their m/z ratio with the ion packets having the smaller m/z ratio experiencing the shortest

DOUBLE REFLECTRON TOF

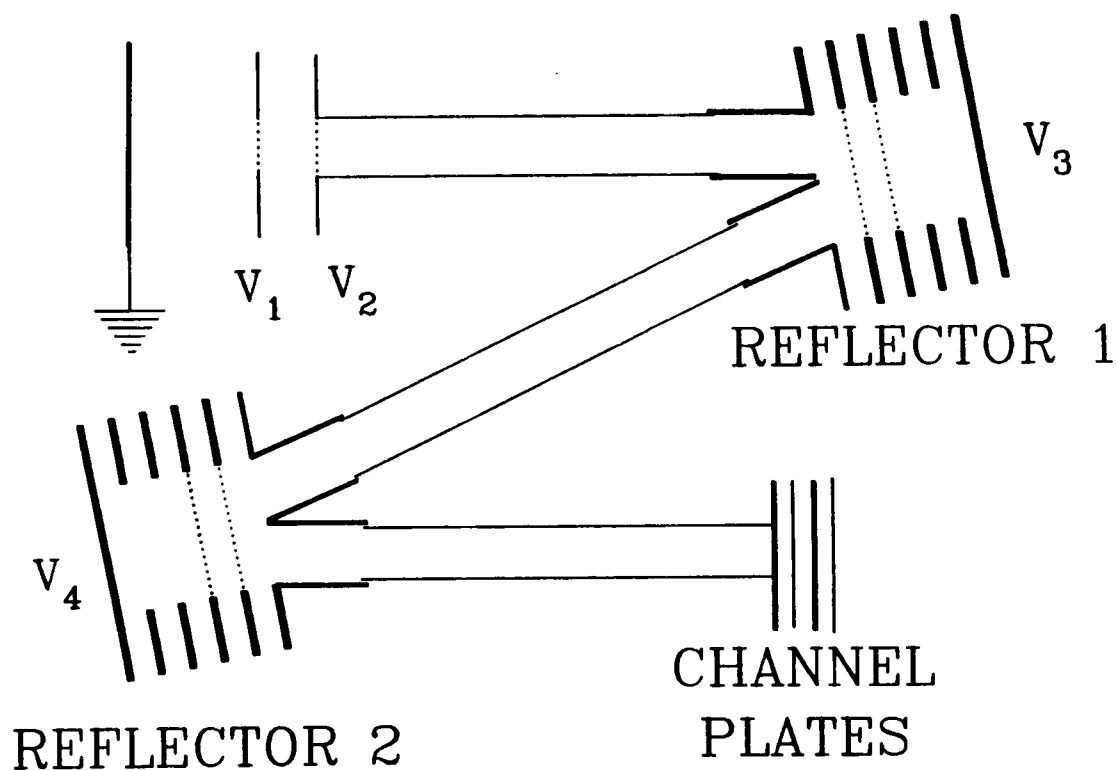


Figure III-18. Schematic of double reflectron time-of-flight mass spectrometer. V_1 and V_2 are the applied voltages on the extraction grid and flight tube, respectively. V_3 and V_4 are the applied voltages on the backing plate on each reflectron.

flight times. The individual ion packets then enter the first ion reflector where they are reflected into a second flight tube, also at voltage V_2 . The purpose of the ion reflector is to reduce time-of-flight spread due to the energy dispersion of the individual ion packets. The spread in the time-of-flight is reduced by the reflectron device since ions with higher energy travel a larger distance in the ion retardation region allowing the slower ions to "catch up". Thus if the voltages and distances in the reflectron are properly arranged, ions of the same mass with different energy will arrive at the same time, thereby increasing the mass resolution. Therefore, ions of different energy but with the same m/z ratio will have the same total flight time in the flight tube and ion reflector and in essence be focused in time and space.

In order to increase the total time-of-flight and to economize space a double reflectron time of flight was employed. After leaving the first reflectron, the ions are further allowed to separate in time through the second flight tube where upon they enter a second ion reflector and finally into a third flight tube also at V_2 . The ions further separate in the third flight tube and finally strike a dual micro-channel plate detector. The signal is sent to a 9301 Ortec pre-amplifier and Ortec timing amplifier. The entire mass spectrum is recorded by a Lecroy Transient Digitizer (9400) and plotted out on a Hewlett Packard Color

Pro pen plotter (7440A).

The ion reflectors consisted of one face plate, four field rings, and one backing plate. The face plate was made out of $1/8$ " stainless steel and was $2\frac{1}{2}$ " in diameter. Two short tubes ($1/2$ " I. D. and approximately $1/2$ " long) were welded in each face plate to support the flight tubes. The flight tubes were made out of $1/2$ " O. D. copper tubing and were 6" long. The short tubes were welded in place such that the central axis was 15° from the normal of the face plate. The complete angle between the flight tubes axis was 30° . The flight tubes were held in the face plate with set screws giving complete flexibility in the flight tube geometry. A Mo wire mesh (90% transmittance, Buckbee-Mears) was spot welded onto the back of each face plate.

The backing plate and field rings were $2\frac{1}{2}$ " in diameter and slotted for three support rods. The field rings were made out of $1/32$ " stainless steel with a $1\frac{1}{2}$ " aperture. The backing plate also was made out of $1/32$ " stainless steel. The first two field rings had a Mo wire mesh (90% transmittance) spot welded over the aperture. The field rings and face plate were connected with $200k\Omega$ vacuum resistors so that the appropriate voltage drop would be experienced across each ring. The whole assembly was held together by 0-80 threaded rods placed through the slots and insulated by ceramic spacers (TU-C-500, Kimball Physics). The field rings were spaced approximately $1/8$ " apart and

insulated from one another by ceramic spacers (SP-C-100, Kimball Physics).

The backing plates had a separate variable negative voltage (V_3 and V_4) applied to them so as to draw the ions further into the reflector. It was found that adjusting these voltages improved the ion signal intensity and helped decrease the width of the ion packets.

With this double reflectron arrangement, the isotopes of xenon could be resolved (figure III-19). The two lesser abundant isotopes were not observed in the spectrum because of the low ion intensity. The resolution at 131 amu was calculated to be approximately 232 (peak width approximately 50ns). It appeared that in the present arrangement the peak widths were limited by the electronics as indicated by the tailing in the mass peaks. This tailing was a result of electronic ringing.

Another limiting factor is the size of the ion reflector itself. The 30° angle of reflection allowed by the ion reflectors described above allowed only approximately $1\frac{1}{2}$ " in depth for the ion turn around. In retrospect, this distance was too short to take full advantage of the mass reflectron. The mass resolution was more than adequate to resolve the $C_nH_n^+$ mass peaks in this experiment.

Typical voltages employed in the experiment were: $V_1 = -880$, $V_2 = -880$, $V_3 = -421$, and $V_4 = -421$. The voltage on the

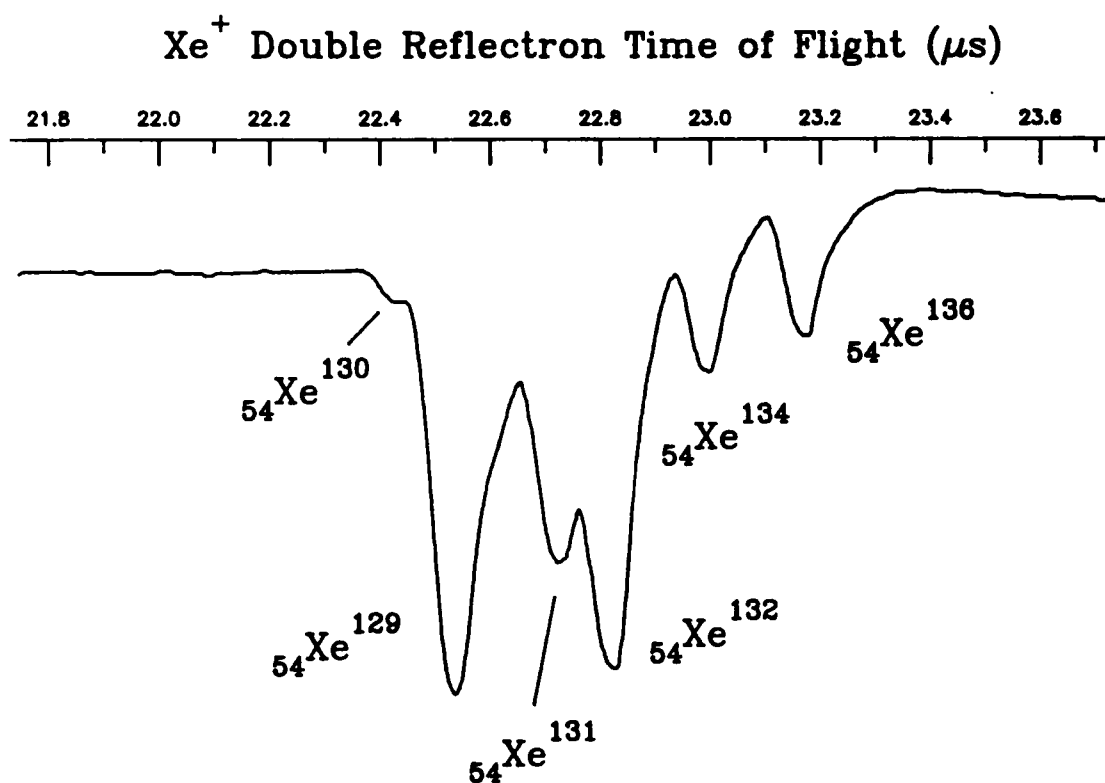


Figure III-19. Mass spectrum of xenon obtained with the double reflectron mass spectrometer. Ions were produced via resonantly enhanced (3+2) MPI of the $6s[3/2]_1$ state. The resolution at this mass is ~ 232 .

channel plates was typically -1900 volts. The experiments were conducted usually at a background pressure of $\geq 10^{-5}$ Torr and at pressures as high as 2×10^{-4} Torr during the experiments.

Ethylene. Figure III-20 shows the resonantly enhanced (3+2) MPI spectrum of ethylene obtained in a molecular beam while tuning the dye laser from 530nm to 485nm. The highest filled molecular orbital is the $2p\pi_x$ orbital with one node.¹⁷¹ In a centrosymmetric atomic system it is anatomically a p orbital ($\ell=1$), Therefore, π -s and π -d transitions are expected in dipole allowed transitions. The observed signals in figure III-20 correspond to transitions of the first Rydberg series in ethylene labeled 2R (π -3d σ). A progression in ν_2 and ν_4 is observed. Assignment of this spectrum is based on the vacuum ultraviolet absorption spectrum obtained by McDiarmid¹⁷¹ and energy-loss spectrum obtained by Ross and Lassettre¹⁷². Figure III-21 shows the resonantly enhanced (3+1) MPI spectrum of ethylene while tuning the dye laser from 435nm to 415nm. Excitation via the 3R (π -3d δ) and 3R'' (π -4s) Rydberg series and their vibrational subbands was found to result in rather sharp MPI signals. Assignment of these transitions are again based on the vacuum ultraviolet absorption spectrum obtained by McDiarmid¹⁷¹ and on the classic work of Mulliken¹⁷³. Excitation spectra were obtained by placing the gate of the

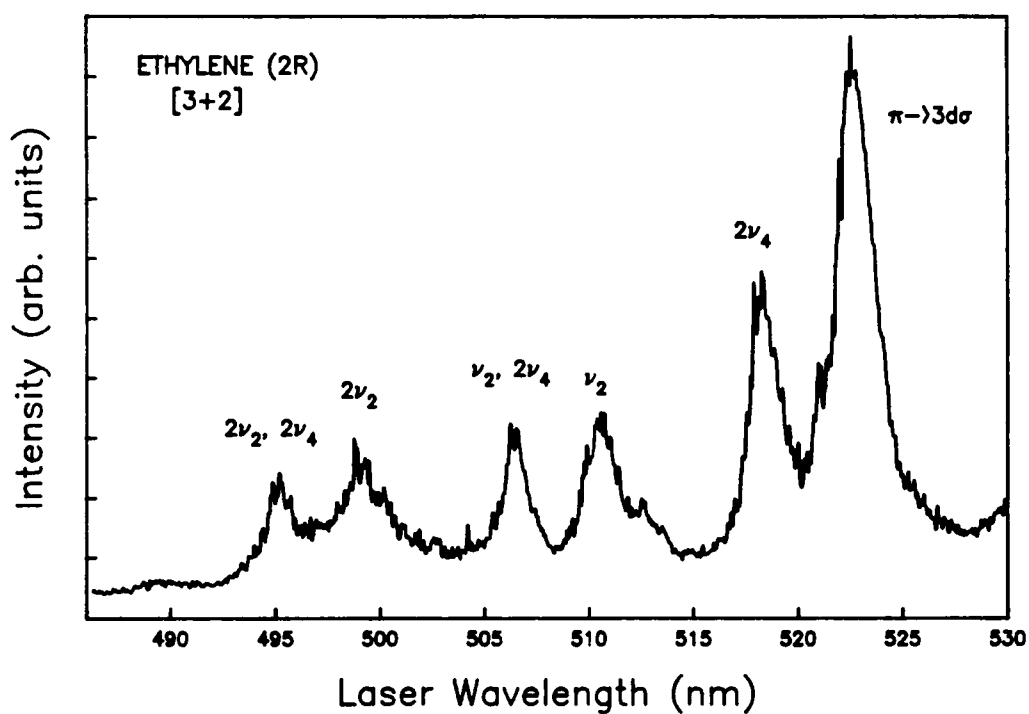


Figure III-20. Resonantly enhanced (3+2) MPI spectrum of ethylene via the 2R Rydberg series as a function of laser wavelength.

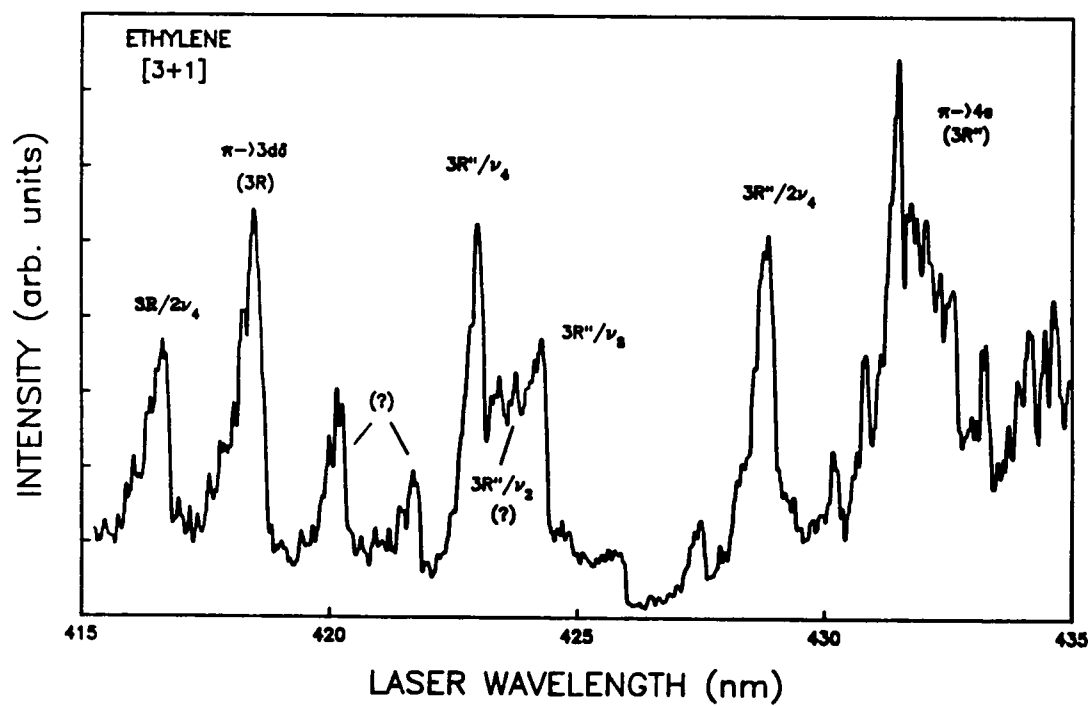


Figure III-21. Resonantly enhanced (3+1) MPI spectrum of ethylene via the 3R and 3R'' Rydberg series as a function of laser wavelength.

boxcar integrator on the $C_2H_2^+$ mass signal in the mass spectrum of ethylene and then scanning the dye laser.

Two other transitions were also observed while tuning through the 3R ($\pi \rightarrow 3d\delta$) and 3R'' ($\pi \rightarrow 4s$) Rydberg vibrational progressions at excitation wavelengths of approximately 420nm and 422nm. These two transitions are labeled (?) in figure III-21. These transitions were not observed in the vacuum ultraviolet absorption spectrum and also were not observed in an MPI cell. The origin of these two transitions is not known at this time. One possibility is that they are transitions associated with third harmonic interference effects since they are only observed in the low pressure of the molecular beam and not in the MPI cell. Third harmonic interference effects have been observed recently in the MPI spectrum of acetylene.^{174,175} In order to examine whether these transitions were associated with third harmonic effects, an experiment in which the pump beam was retro-reflected upon itself in the MPI cell was performed. Retro-reflection of the laser beam failed to reproduce these signals arguing against an interference effect.

Another possible origin of these bands is that they are the result of three-photon allowed transitions which would explain their absence in the single-photon vacuum ultraviolet absorption spectrum. Ashfold et al.¹⁷⁶ observed such a Rydberg series in acetylene. The excited state

symmetry of this Rydberg series in acetylene is ${}^1\Phi_u$. This state results from electronic transitions with $\Delta\Lambda=3$. A similar excited state that was only observed in a three-photon excitation process has been reported in ammonia.¹⁷⁷ Further work, including theoretical calculations, needs to be done in order to characterize these features in the MPI spectra.

The photoelectrons that resulted from resonantly enhanced MPI via the Rydberg series reported above were monitored. Although energy analysis of the photoemitted electrons was somewhat onerous, there is evidence that ionization through the 2R vibrational levels follow the $\Delta v=0$ propensity rule expected of Rydberg state photoionization. Ionization through the 2R (0-0) transition results in ions in the vibrational ground state of the ion. Photoelectron signals from the other 2R vibrational levels were too weak to be measured. The energy spectra of molecules was calibrated against energy spectra of xenon or nitric oxide.

Because of the low electron signals observed in these PES studies, a small "pusher voltage" (~ 2 volts) was applied to a plate parallel to the entrance aperture, to help increase the photoelectron signal, especially for the low energy electrons. Table III-12 lists the measured (corrected for applied pusher voltage) and calculated kinetic energies of the photoemitted electrons of the various transitions and their respective three-photon

Table III-12. Measured and calculated photoelectron energies for ethylene and butadiene. The assignments are based on the works of McDiarmid,¹⁷¹ Johnson,¹⁷⁹ and Mulliken.¹⁷³

STATE ASSIGNMENT	RESONANT EXCITATION ENERGY	(n+m)	CALCULATED ENERGY (eV)	OBSERVED ENERGIES (eV)
<u>ETHYLENE</u>				
2R (π -3d σ)	57350cm ⁻¹	(3+2)	1.34	0, ~1, 1.3
2R 2v ₄	57837cm ⁻¹	(3+2)	1.41	0, ~1
2R v ₂	58720cm ⁻¹	(3+2)	1.45	0
2R v ₂ , 2v ₄	59206cm ⁻¹	(3+2)	1.50	0
2R 2v ₂	60096cm ⁻¹	(3+2)	1.57	-
2R 2v ₂ , 2v ₄	60496cm ⁻¹	(3+2)	1.59	-
3R'' (π -4s)	69509cm ⁻¹	(3+1)	0.99	0, ~1
3R'' 2v ₄	70061cm ⁻¹	(3+1)	1.01	0, ~1
3R'' v ₃	71090cm ⁻¹	(3+1)	1.09	0, ~1
? ?	71452cm ⁻¹	?	?	0, ~1
3R (π -3d δ)	71787cm ⁻¹	(3+1)	1.36	0, ~1, 1.4
3R 2v ₄	72167cm ⁻¹	(3+1)	1.37	0, ~1
4R'' (v-5s)	78358cm ⁻¹	(3+1)	2.44	2.44
<u>BUTADIENE</u>				
4R ₁ (π -3p σ)	66036cm ⁻¹	(3+1)	1.82	0, ~1, 1.82
4R ₂ (π -4p σ)	64548cm ⁻¹	(3+1)	1.58	0, ~1, 1.58
4R* ?	66182cm ⁻¹	(3+1)	1.85	0, ~1, 1.85
(π -5s)	66616cm ⁻¹	(2+1)	3.4	3.4

excitation energy. Figure III-22 shows the photoelectron energy spectra of the 3R (0-0) transition taken with an applied "pusher voltage" of -2 volts. Photoelectrons are observed leaving the ion in the ground vibrational state as expected. In addition, photoelectrons were observed at near "zero" kinetic energy and at approximately 1 eV. The origin of these electrons is unknown since they cannot be assigned to known ethylene vibrational frequencies of the ion. The photoelectron signal at 1 eV is present only when the molecular beam is present and when the laser is tuned to a resonance. Furthermore, ions with masses corresponding to $C_2H_2^+$ i. e., originating from ethylene, were present in figure III-23. "Zero" energy electrons are present when the molecular beam is off but are much less intense (<20 times). It was concluded that some small fraction of slow electrons were due to background gas and the majority being due to ethylene, since the hydrocarbon studies were conducted at higher pressures than the atomic studies (10^{-5} Torr as opposed to 10^{-6} Torr). Since the electrons at 1 eV are present only when the molecular beam is on and when ionization of ethylene is occurring it is possible that these electrons are a result of a secondary electron source such as scattering off of a surface. This explanation is only suggested since their presence cannot be easily attributed to an expected ionization process in ethylene. Similar 1 eV electrons are observed in butadiene as

PHOTOELECTRON SPECTRA OF ETHYLENE

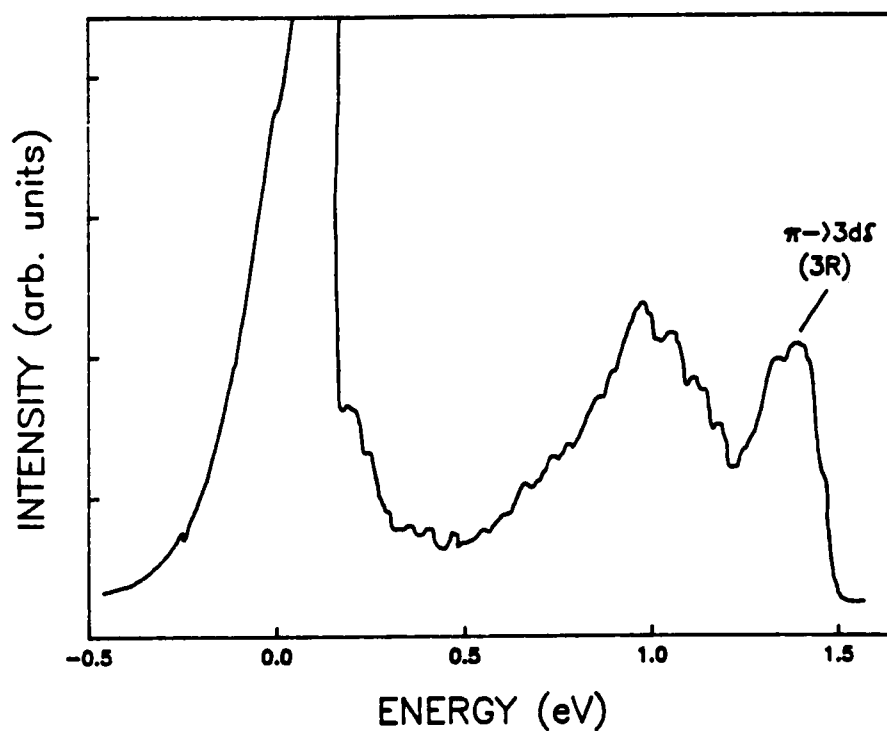


Figure III-22. Photoelectron energy spectrum of photoemitted electrons from resonantly enhanced (3+1) MPI via the 3R (ν_{00}) transition of ethylene.

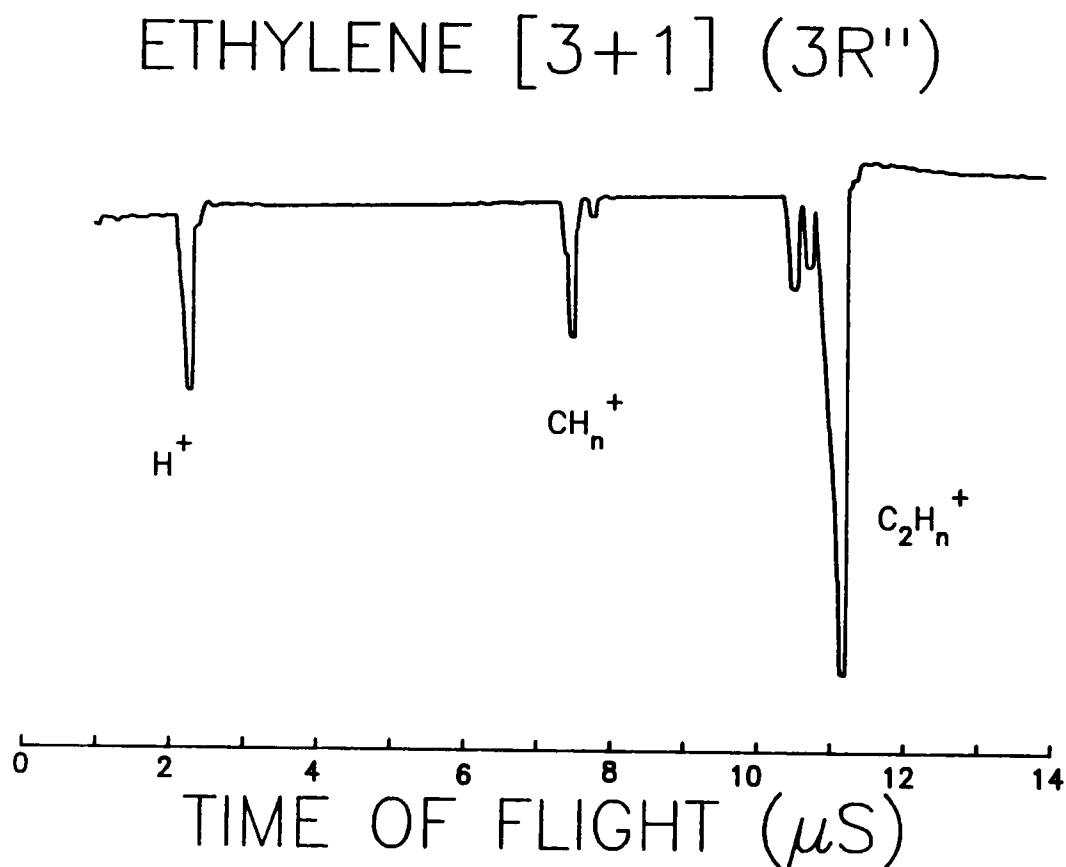


Figure III-23. Observed mass spectrum that results when exciting the $3R''$ (ν_{00}) state of ethylene.

presented below.

Photoelectrons that result from resonantly enhanced MPI via the $3R''$ (0-0) transition show a deviation from the $\Delta v=0$ propensity rule. Photoelectrons producing ions in the vibrational ground state as well as ions with one quanta of vibrational excitation of ν_3 (1215cm^{-1}) are observed (figure III-24). This photoelectron signal was intense enough to measure the angular distribution of the photoelectrons corresponding to leaving the ion in the ground state. Since the photoionization occurs from a s ($\ell=0$) type orbital, the angular distribution is expected to follow as $\cos^2\theta$. Figure III-25 shows that the measured angular distribution roughly follows a $A + B\cos^2\theta$ distribution. Figure III-25 shows that the angular distribution is rather convoluted, displaying some structure. This structure is probably the result of interference of the out going waves since the $3R''$ is not a pure s type Rydberg state as evidenced by the photoelectron energy spectrum. Table III-13 lists the β_{2i} coefficients for the Legendre polynomial fit of the experimental data for the $3R''$ state of ethylene.

trans-1,3-Butadiene. The highest filled molecular orbital for trans-1,3-butadiene (C_4H_6), is the $2p\pi$ (b_g) orbital possessing two nodal planes. Hence in a centrosymmetric atomic system the orbital is essentially a d ($\ell=2$) type orbital. Therefore, the resulting selection

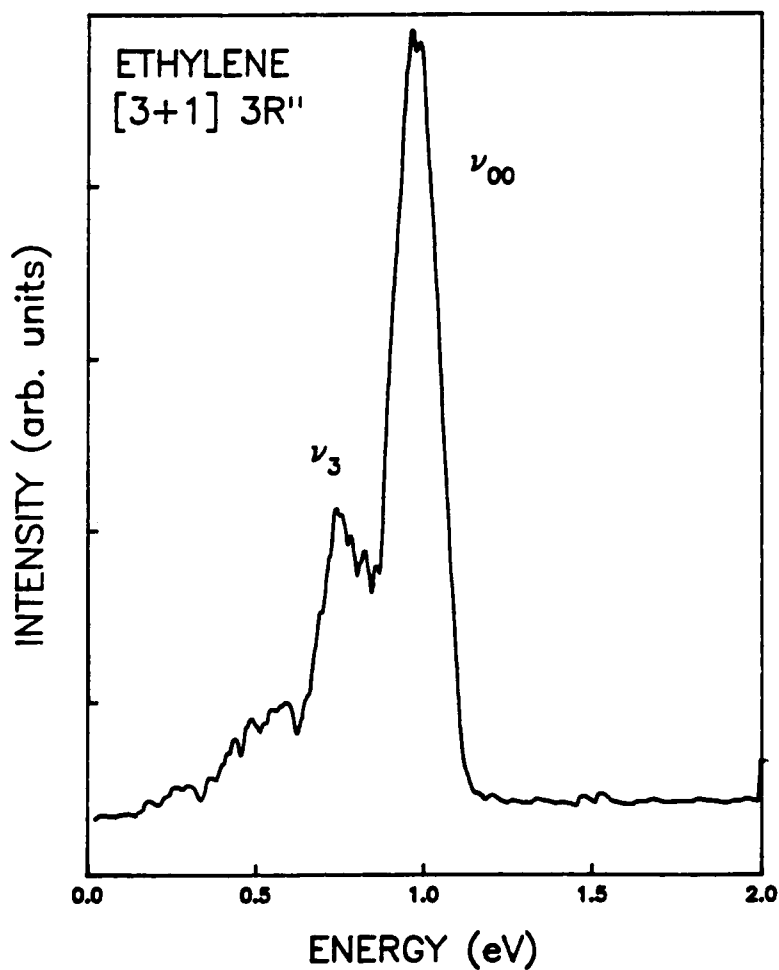


Figure III-24. Photoelectron energy spectrum of photoemitted electrons from resonantly enhanced (3+1) MPI via the 3R'' (ν_{00}) transition of ethylene.

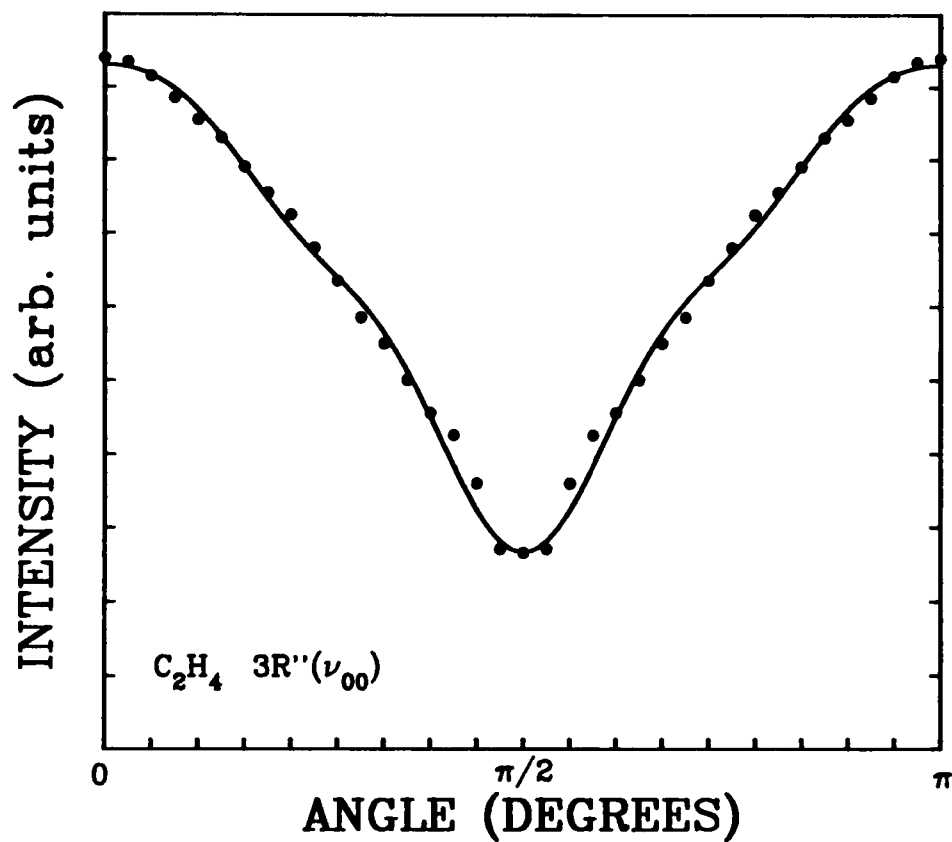


Figure III-25. Photoelectron angular distribution from resonantly enhanced (3+1) MPI via the 3R'' (ν_{00}) transition of ethylene.

Table III-13. β_{2i} coefficients for Legendre polynomial fit to experimental data of angular distribution of photoemitted electrons via resonantly enhanced (3+1) MPI of the $3R'' \nu_{00}$ of ethylene.

STATE	$\beta(0)$	$\beta(2)$	$\beta(4)$	$\beta(6)$	$\beta(8)$
$C_2H_4 \ 3R'' \nu_{00} \ [3+1]$	1	0.756	-0.178	0.176	-0.073

rules allow for $2p\pi$ -np and $2p\pi$ -nf dipole transitions but forbid $2p\pi$ -ns and $2p\pi$ -nd transitions.¹⁷⁸ Tuning the laser from 460nm to 431nm produced a rich excitation spectrum of three photon allowed transitions identical to that observed by Johnson.¹⁷⁹ In this tuning range, a number of Rydberg series and their vibrational subbands were observed. Essentially, the same resonantly enhanced MPI excitation spectrum was obtained in the MPI cell. No new or unassignable transitions were observed. We also tried to investigate the two-photon allowed 5s Rydberg series of trans-1,3-butadiene. Only the (0-0) transition of the 5s Rydberg was observed. The 5s Rydberg vibrational progression was not able to be observed because the dye used (rhodamine 610) in the dye laser did not extend out far enough (< 598nm) to probe these levels. The 5s Rydberg vibrational progression has been previously observed using MPI.¹⁸⁰

The mass spectrum of resonantly enhanced MPI of trans-1,3-butadiene (figure III-26) showed extensive fragmentation. Little or no parent mass peak was observed at a number of different pumping frequencies. The most intense mass signals observed were C^+ and $C_2H_2^+$. Excitation spectra were taken by placing the gate of the boxcar integrator on either of these mass signals and scanning the dye laser. Similar extensive fragmentation has been observed in two-color laser studies of trans-1,3-butadiene

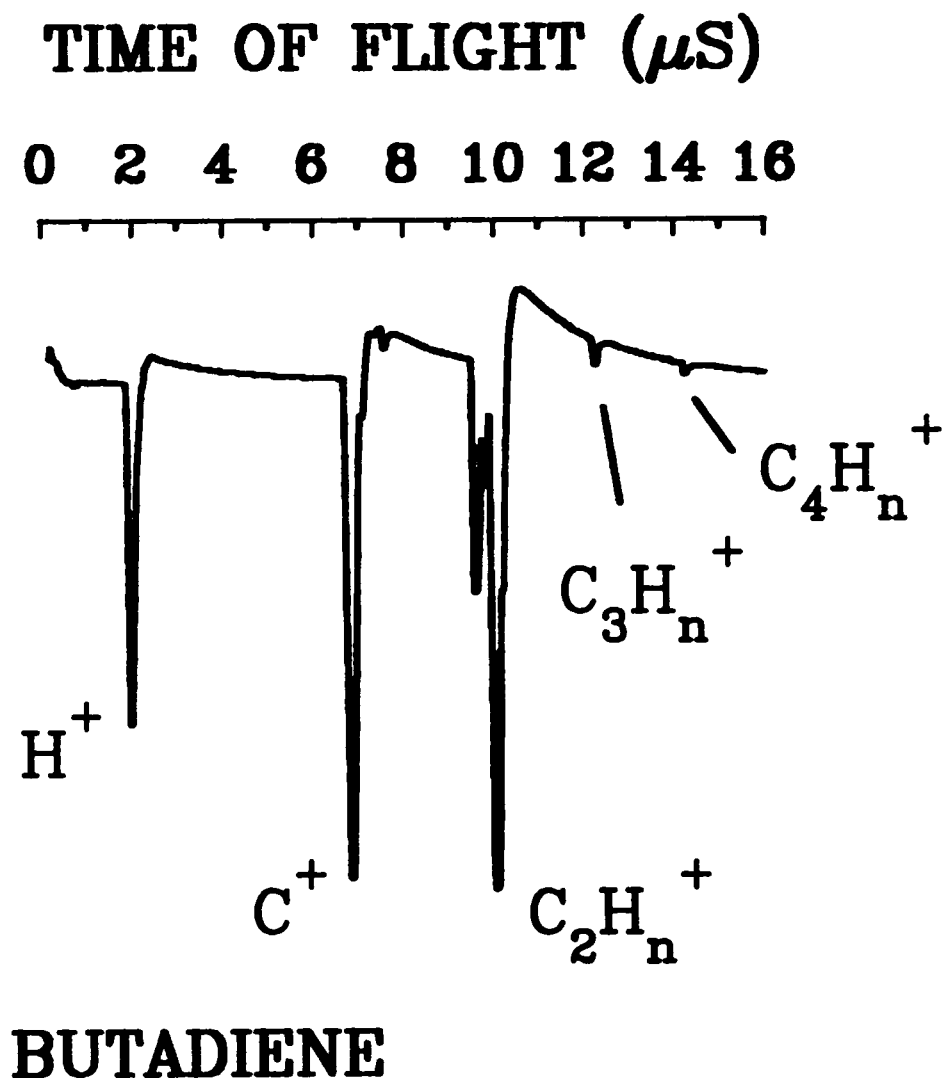


Figure III-26. Resonantly enhanced (2+1) MPI mass spectrum of 1,3-trans-butadiene via the 5s Rydberg state.

by Woodward et al.¹⁸¹

The energies of the photoelectrons that resulted from resonantly enhanced MPI of trans-1,3-butadiene were monitored as in the case of ethylene. In some instances, photoelectrons were not observed because of weak signals. A "pusher voltage" was again applied to help increase the photoelectron signal. "Zero" energy electrons and electrons with 1 eV of energy were again observed in the energy spectrum. Table III-12 lists the measured (with an applied voltage) and calculated kinetic energies of the photoemitted electrons of the various transitions and their respective three-photon excitation energy. The most intense signals were observed from the (0-0) transitions. Photoelectrons from resonantly enhanced (3+1) MPI via the (0-0) transitions corresponded to leaving the ions in their respective ground vibrational states as expected. The photoelectron energy spectrum for resonantly enhanced (2+1) MPI via the 5s (0-0) state is shown in figure III-27. Only one photoelectron peak is observed corresponding to leaving the ion in the ground vibrational state. The photoelectrons at higher energy are extraneous and do not reproduce from scan to scan. In all studies, the photoelectron signals were too low to measure angular distributions.

In summary, several Rydberg series of ethylene and trans-1,3-butadiene were investigated using resonantly enhanced MPI-PES. Extensive fragmentation was observed in

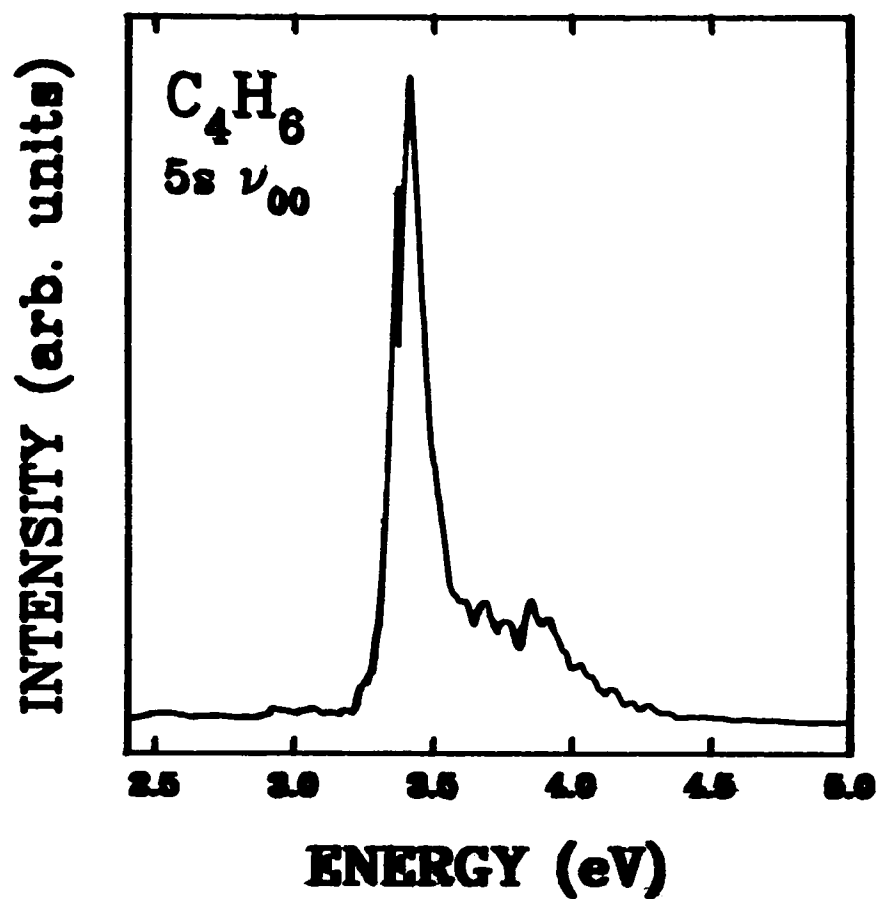


Figure III-27. Photoelectron energy spectrum of photoemitted electrons from resonantly enhanced (2+1) MPI via the 5s Rydberg state of 1,3-trans-butadiene.

the mass spectra for both molecules. In addition, energy analysis of the photoelectrons demonstrated that Franck-Condon factors are observed in the multiphoton ionization process. Photoelectrons at near "zero" energy and 1 eV are observed in both PES spectra of ethylene and trans-1,3-butadiene. The origin of these electrons remains a mystery but probably results from the extensive fragmentation of neutrals followed by photoionization that is observed from the hydrocarbons or through the absorption of additional photons of the parent ion which rapidly dissociates. The latter is probably the most likely mechanism since energy analysis shows that the parent ion is formed.

"Zero" energy electrons have also been observed in resonantly enhanced MPI via the $A\ ^2\Sigma^+$ ($v'=0, 1, 2$) levels of nitric oxide by Miller and Compton.¹⁸² These authors discuss possible mechanisms for the origin of "zero" energy electrons in nitric oxide which include photoionization via autoionizing states and the possible role of accidental resonances.

ArNO. The van der Waals complex of nitric oxide and argon has been investigated by two-photon resonant three-photon ionization via the $C\ ^2\Pi$ state of the complex formed between the Ar ground state and the NO $C\ ^2\Pi$ ($v'=0$) state. The purpose of this study was to investigate the effect of the Ar atom on the outgoing electron and determine if the

angular distribution was different for ArNO as compared to pure NO. The geometry of the complex is T-shaped with the 3p type, Rydberg orbitals of the $C^2\Pi$ state normal to the plane of the NO bond.¹⁸³

The ArNO van der Waals complex was formed by using a 5% mixture of NO in argon in a supersonic expansion. It was found that formation of ArNO was dependent on background pressure in the vacuum chamber, backing pressure of the NO - argon gas mixture, and the delay of the nozzle pulse with respect to the laser pulse. If the background pressure in the chamber was high ($\geq 10^{-5}$ Torr), then the ArNO complex would not be observed due to collisions with background molecules in the chamber. Likewise, if the backing pressure (pressure behind the nozzle) wasn't sufficiently high (> 5 p.s.i), sufficient clustering of ArNO would not take place in the nozzle expansion. The most intense ArNO signal was observed when the leading edge pulse of the nozzle occurred at the beginning of the laser pulse.

Figure III-28 shows the excitation spectrum of the ArNO complex. It was recorded by placing the gate of the boxcar on the $ArNO^+$ peak (observed in the linear time-of-flight mass spectrum) and tuning the dye laser. Four resonances were observed corresponding to the lowest vibrational levels of the $C^2\Pi$ state of the ArNO complex. The apparent structure in the excitation spectrum could possibly be due to stretching or bending vibrational modes or rotational

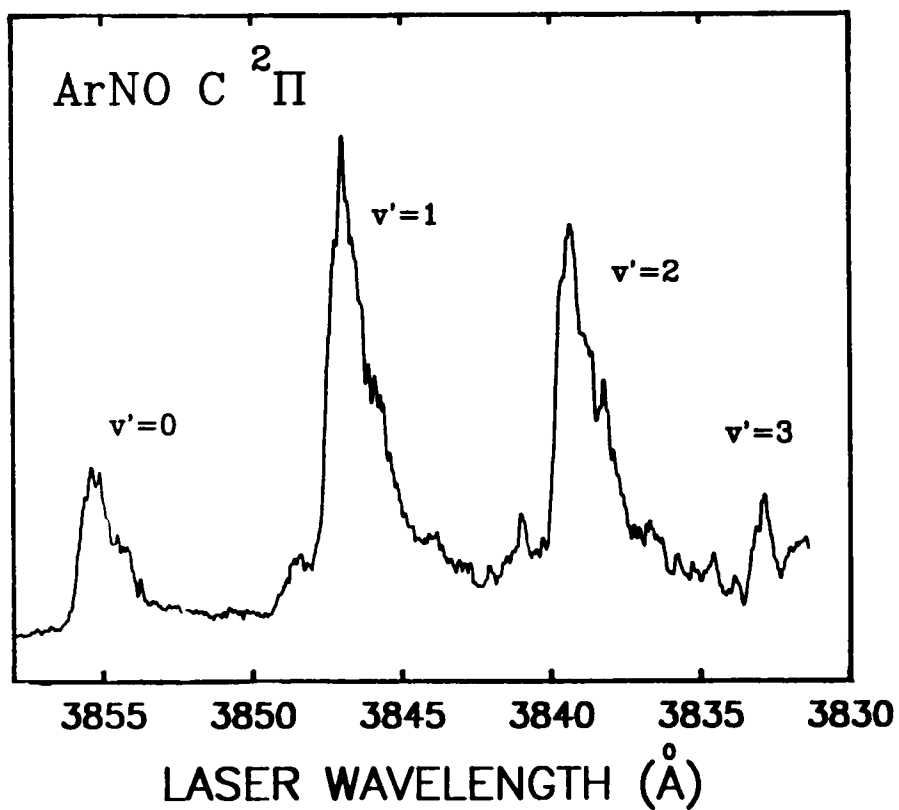


Figure III-28. Resonantly enhanced (2+1) MPI spectrum of ArNO via the C $^2\Pi(v'=0,1,2,3)$ state.

bands. The two-photon resonance frequencies of the ArNO C $^2\Pi$ state are listed in table III-14. The vibrational excitation frequencies are similar to those observed by Sato et al.¹⁸³ and Miller et al.¹⁸⁴ The 0-0 transition of the ArNO C $^2\Pi$ state is shifted by $\sim 335\text{cm}^{-1}$ from the corresponding NO transition. This shift represents the difference between the excited and ground state potential well depths.¹⁸⁴ Since the ground state well depth of ArNO is given as approximately 118cm^{-1} ¹⁸³, the dissociation energy of the ArNO C $^2\Pi$ state is estimated to be approximately 453cm^{-1} . This value is similar to that obtained by Miller et al.¹⁸⁴

Figure III-29 shows the time-of-flight mass spectrum that results when the laser is tuned to the C $^2\Pi(v'=1)$ state of ArNO. Only two signals are observed in the mass spectrum at this frequency. The mass signal at $\sim 6.5\mu\text{S}$ corresponds to NO^+ and the signal at $\sim 10\mu\text{S}$ corresponds to ArNO^+ . When the pump laser was tuned off resonance, only the NO^+ signal was present. NO^+ is probably the result of three-photon nonresonant multiphoton ionization. Nonresonant multiphoton ionization in NO has been extensively studied by Carman and Compton.¹⁸⁵

Photoelectron energy spectra were obtained by tuning the laser to the resonances observed in figure III-28 and monitoring the energy of the resulting electrons. The measured kinetic energies of the photoemitted electrons are given in table III-14. In all cases, a single photoelectron

Table III-14. Measured energies for photoelectrons from resonantly enhanced (2+1) MPI of ArNO via the $C^2\Pi$ ($v'=0, 1, 2, 3$) state and resonantly enhanced (2+1) MPI of NO via the $C^2\Pi$ ($v'=0$).

$v' \leftarrow v''$	TWO-PHOTON ENERGY	LASER WAVELENGTH	I.P.	K.E.
<u>ArNO</u>				
0 $\leftarrow$ 0	52,038 cm^{-1}	384.33 nm	9.148 eV	0.53 eV
1 $\leftarrow$ 0	52,095 cm^{-1}	383.91 nm	9.148 eV	0.54 eV
2 $\leftarrow$ 0	52,148 cm^{-1}	383.52 nm	9.148 eV	0.55 eV
3 $\leftarrow$ 0	52,192 cm^{-1}	383.20 nm	9.148 eV	0.56 eV
<u>NO</u>				
0 $\leftarrow$ 0	52,373 cm^{-1}	381.87 nm	9.246 eV	0.49 eV

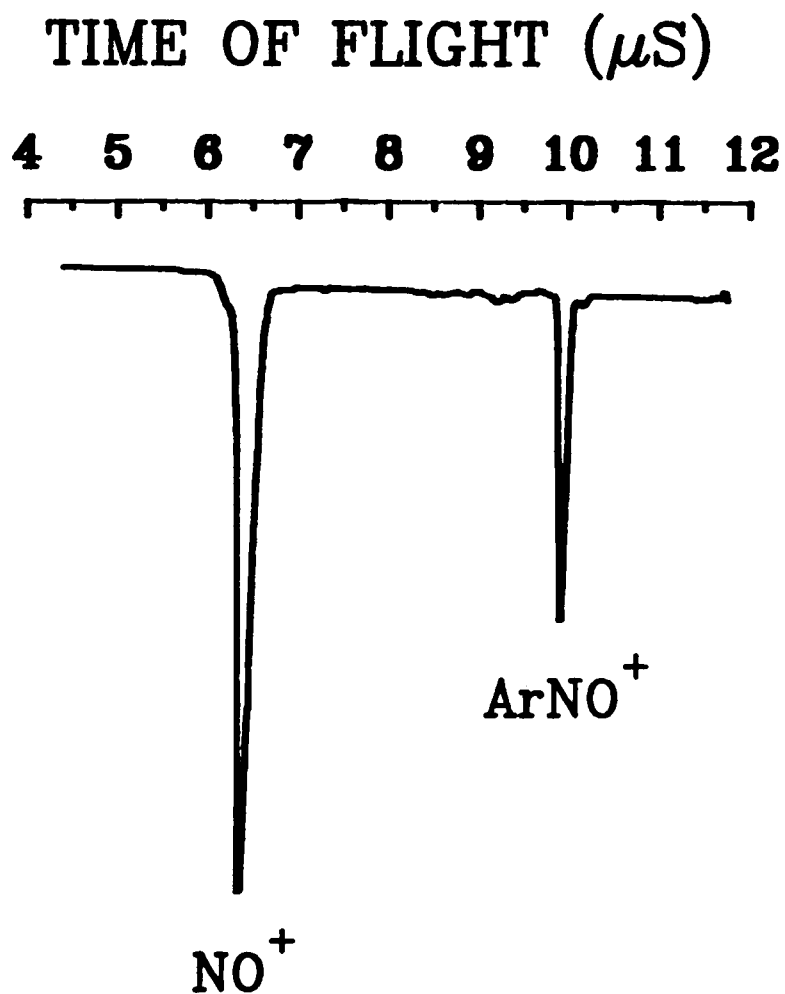


Figure III-29. Mass Spectrum of ArNO van der Waals complex

peak was observed, with its energy given by equation III-2, corresponding to the production of ArNO^+ ion produced in the ground vibrational level following the $\Delta v=0$ propensity rule. These results are similar to that observed by Sato et al.¹⁸⁴

Angular distributions of the photoemitted electrons from the $\text{ArNO } C^2\Pi$ state were measured employing the same procedure as described earlier. The $\beta(2i)$ coefficients from the Legendre polynomial fit of the experimental data are presented in table III-15 for the $\text{ArNO } C^2\Pi(v'=0,1,2)$ state along with the $\beta(2i)$ coefficients of the Legendre polynomial fit of the angular distribution of a rotational level in the $C^2\Pi(v'=0)$ state of pure NO. Measurement of the angular distribution from the $v'=3$ vibrational level of ArNO was not possible because of the low intensity of the photoelectron signal.

The measured angular distributions of the photoemitted electrons from all three vibrational levels of $\text{ArNO } C^2\Pi$ were nearly identical and exhibited a $A + B\cos^2\theta$ distribution as indicated by the Legendre polynomial fit which requires only the $\beta(2)$ term. The measured angular distribution from pure NO also was proportional to $A + B\cos^2\theta$ but had a higher minimum at 90° than the measured angular distributions from $\text{ArNO } C^2\Pi(v'=0,1,2)$. To the best of our knowledge, these are the first reported angular distributions of photoelectrons from a van der Waals complex.

Table III-15. β_{2j} coefficients for Legendre polynomial fit of experimental data for resonantly enhanced (2+1) MPI via the ArNO $C^2\Pi$ ($v'=0, 1, 2, 3$) state and NO $C^2\Pi$ ($v'=0$) state.

	<u>$\beta(0)$</u>	<u>$\beta(2)$</u>	<u>$\beta(4)$</u>	<u>$\beta(6)$</u>
<u>ArNO</u>				
0 $\leftarrow$ 0	1	0.8929	6.6094E-02	-5.1754E-02
1 $\leftarrow$ 0	1	0.8764	7.6232E-02	-0.0542
2 $\leftarrow$ 0	1	0.8969	6.1482E-02	-3.264E-02
3 $\leftarrow$ 0			SIGNAL TOO WEAK	
<u>NO</u>				
QZ1 $\leftarrow$ QY2	1	0.7273	5.5095E-02	-4.4393E-02

Figure III-30 shows the angular distributions of the photoemitted electrons from the $\text{ArNO } C \ ^2\Pi(v'=0)$ and $\text{NO } C \ ^2\Pi(v'=0)$ states. Although a small difference is observed between the two distributions, it is seen that the presence of the Ar atom has no major effect on the outgoing electron. The deBroglie wavelength of the outgoing electron is calculated to be approximately $17\text{\AA}$ which is about four times the bond length of the $\text{ArNO } C \ ^2\Pi$ excited state.¹⁸⁶ Therefore, any electron scattering off of the Ar atom is expected to be minimal. More photoelectron angular distribution measurements, from other excited states of ArNO , are needed to be taken in order to draw any conclusions about the effect of the rare gas atom on the outgoing electron.

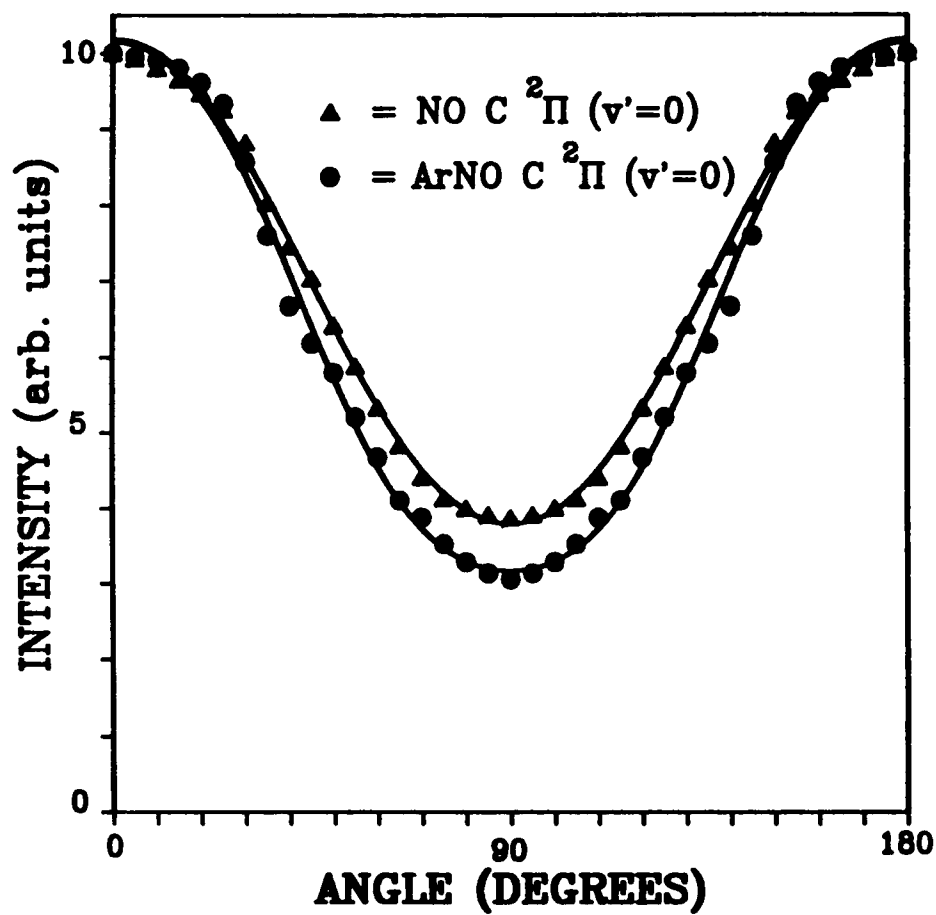


Figure III-30. Photoelectron angular distribution for resonantly enhanced (2+1) MPI via the C $^2\Pi(v'=0)$ of ArNO (●) and via the C $^2\Pi(v'=0)$ of NO (▲).

Chapter IV

Optical Processes in Alkalies

Introduction

The interaction of intense coherent radiation (lasers) with metal vapors has lead to a number of interesting nonlinear optical processes. A few examples of these processes include self focusing,^{187,188} optically pumped stimulated emission (OPSE),¹⁸⁹⁻¹⁹² stimulated electronic Raman scattering (SERS),¹⁹³⁻¹⁹⁵ stimulated hyper-Raman scattering (SHRS),¹⁹⁶⁻¹⁹⁸ and various four and six wave-mixing processes.¹⁹⁹⁻²⁰¹ Reviews covering these and various other non-linear processes can be found in many textbooks on the subject.²⁰²⁻²⁰⁵

In this chapter observations of several non-linear optical processes are reported upon multiphoton excitation of lithium, sodium, and potassium vapor. Most of the processes studied involve four wave-mixing. As a basis for discussion of the experimental results, the theory of four wave-mixing processes is presented.

In classical linear optics the induced polarization of an optical medium is linearly related to the applied electric field by

$$\vec{P} = \epsilon_0 \chi^{(1)} \vec{E} , \quad (\text{IV-1})$$

where $\chi^{(1)}$ is the linear susceptibility of the medium and ϵ_0 is the dielectric constant. With the high electric fields associated with lasers, higher orders of E must be considered. The induced dielectric polarization can now be expressed as

$$\vec{P} = \epsilon_0 [\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots] . \quad (\text{IV-2})$$

If a monochromatic plane wave of frequency ω , propagating through a non-linear medium is considered, it can be shown that the quadratic expression, $\chi^{(2)} E^2$, in the induced non-linear polarization, contains a term oscillating at a frequency 2ω , the cubic expression, $\chi^{(3)} E^3$, contains a term oscillating at a frequency 3ω , and so on. The generation of these harmonic frequencies is known as second harmonic generation and third harmonic generation, respectively.

The susceptibilities $\chi^{(i)}$ have tensor properties with components that depend on the symmetry properties of the optical medium. For example, gases and liquids which are spatially isotropic do not show any second-order nonlinear response because all even-order susceptibilities are zero in media with inversion symmetry. The dominant response comes from the odd-order terms. Likewise, solids with a center of inversion (e. g. NaCl) also will not show any second-order response. Solids that are centro-symmetric exhibit a second

order non-linear response (e. g. KHP).

In a parametric four wave-mixing process where two laser photons of the same frequency ω_l , propagate through a non-linear medium, the induced non-linear polarization acts as a source of new waves at frequencies $2\omega_l = \omega_1 \pm \omega_2$ which propagate along the laser beam axis. These waves travel at different phase velocities throughout the medium. The different phase velocities arise from the different refractive indexes for the incident and generated frequencies in the non-linear medium. In order to get appreciable intensity of ω_1 and ω_2 , the phase velocities of the incident and generated waves must be properly phase matched. This "phase-matching" condition may be interpreted as momentum conservation and can be written in a wavevector relation as

$$2\vec{k}(\omega_l) = \vec{k}(\omega_1) \pm \vec{k}(\omega_2). \quad (\text{IV-3})$$

The magnitude of k is $\omega_i \eta_i / c$, where η_i is the index of refraction at ω_i and c is the speed of light in a vacuum. η_i can be calculated from the well known Sellmeiers equation²⁰⁵

$$\eta_i(\omega) \approx \eta(\omega) - 1 \approx Nr_e \sum_i \frac{f_i}{\omega_i^2 - \omega^2}, \quad (\text{IV-4})$$

where N is the atomic number density, f_i is the oscillator strength of the i th transition and $r_e = 2.818 \times 10^{-13} \text{cm}$.

Figure IV-1 qualitatively shows how the refractive index

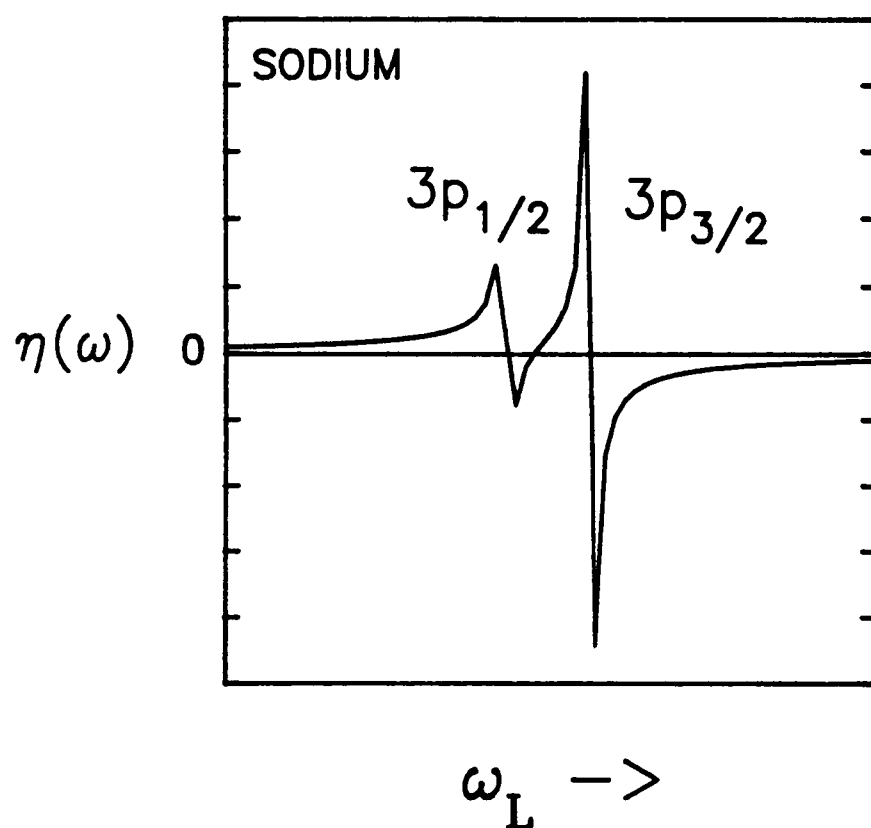


Figure IV-1. Qualitative representation of the behavior of the refractive index as a function of laser frequency.

changes as a function of laser frequency in the vicinity of the $3p\ ^2P_{3/2,1/2}$ fine structure levels of sodium. It is important to note that near a resonance, the refractive index can go from being positively dispersive to being negatively dispersive.

In a parametric four wave-mixing process of the type $\omega_2 = 2\omega_L - \omega_1$ the induced polarization is given by

$$\vec{P}(\omega_2) = \epsilon_0 \chi^{(3)}(-\omega_2, \omega_L, \omega_L, -\omega_1) E_L^2 E_1, \quad (\text{IV-5})$$

where $\chi^{(3)}$ is the third order susceptibility of the process. $\chi^{(3)}$ is given by

$$\chi^{(3)}(-\omega_2, \omega_L, \omega_L, \omega_1) = \frac{1}{3} \frac{(ea_0)^4}{(\hbar c)^3} \sum_{ijk} \frac{\mu_{gi} \mu_{ij} \mu_{jk} \mu_{kg}}{(\Omega_i - \omega_L)(\Omega_j - \omega_{2L})(\Omega_k - \omega_2)}, \quad (\text{IV-6})$$

where μ_{jk} is the electric dipole matrix element between levels j and k , g denotes the ground state, a_0 is the atomic Bohr radius, and $\Omega_i = (E_i - E_g)/\hbar - i\Gamma_i$. The intensity of ω_2 can be expressed as²⁰⁵

$$I_{\omega_2} \propto N^2 |\chi^{(3)}|^2 I_{\omega_L}^2 I_{\omega_1}. \quad (\text{IV-7})$$

From equation IV-7, the intensity of ω_2 is proportional to the square of $\chi^{(3)}$. As can be seen from equation IV-6, the magnitude of $\chi^{(3)}$ increases when the incident frequencies are degenerate with resonances in the medium. The damping term, $-i\Gamma_i$, in Ω_i removes the zero in the resonance denominator and keeps the resonant enhancement finite. This

is known as resonant enhancement. In this particular example, resonant enhancement can occur at either the first-photon level, second-photon level, or at both levels. Analogous expressions can be extended to six wave-mixing processes.

Experimental

Studies in dense alkali vapors were carried out using the apparatus depicted in figure IV-2. The second harmonic of a pulsed Nd:YAG laser (532nm) was used to pump a tunable dye laser. The dye laser operated at 10 Hz with pulses of 8ns duration and average power output of 50-150mW as measured with a Coherent Model 210 power meter. The tunable dye laser output was focussed by means of an optical telescope into the center of a heat pipe oven. The optical telescope consisted of a 200mm fused quartz lens followed by a 45mm aspheric lens to condense the laser output with minimum loss in laser power.

The design of the heat pipe oven is similar to that described by Vidal and co-workers.^{206,207} A schematic of a typical heat pipe is shown in figure IV-3. The heat pipe used in these studies was made out of a one inch diameter stainless steel pipe with an active region of about 25 cm. The entrance window was made out of Quartz. The output

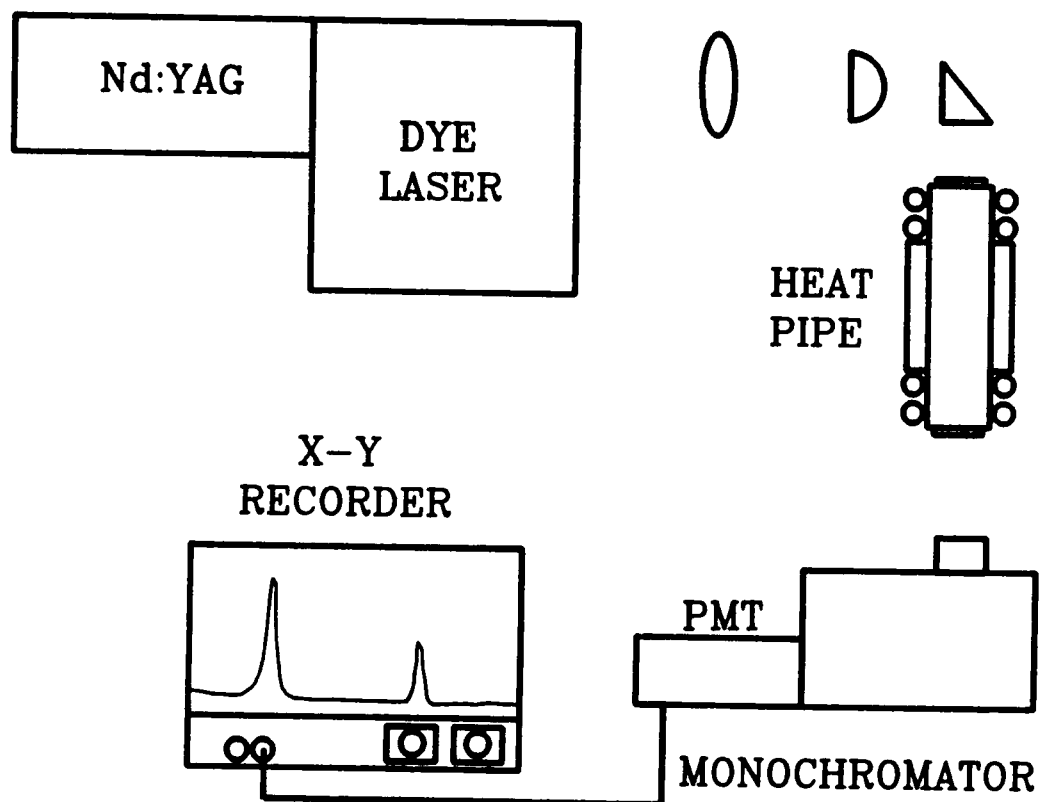


Figure IV-2. Schematic of experimental apparatus used in the study of alkali vapors.

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OPTICAL HEAT PIPE

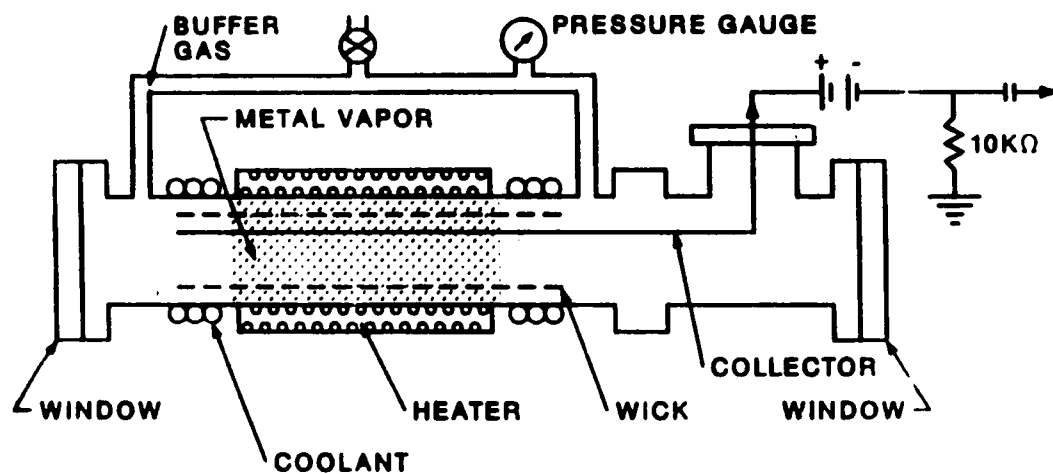


Figure IV-3. Schematic of heat pipe oven.

window was made out of sapphire to allow both visible and infrared radiation to pass through. The ends of the heat pipe were cooled by water circulating through copper tubes in thermal contact with the stainless steel pipe. The alkali was placed in the center of the heat pipe and argon was added as a buffer gas to the desired operating pressure. The purpose of the buffer gas is to confine the alkali vapor and prevent fogging of the windows. The heat pipe generally was operated in the pressure range from 0.5 Torr to 10 Torr (monitored by a Hastings pressure gauge model DV-100).

A heater is used to evaporate the alkali, whereupon it moves toward the ends of the heat pipe where it condenses at the cooling coils. The liquid alkali is then drawn back in the center of the heat pipe by capillary action by means of a "wick" made out of stainless steel mesh. In the evaporation process, the buffer gas is pushed out of the central region of the heat pipe. During heat pipe operation, the alkali follows its own vapor pressure vs. temperature plot. After a period of time an equilibrium is established between the alkali vapor and the buffer gas. Thus, the vapor pressure of the alkali is equal to that of the buffer gas. The alkali vapor temperature is approximately that of the wall of the heat pipe. At the low pressures of these experiments, the metal vapor density may be approximated by the ideal gas law,

$$\frac{n}{V} = \frac{P}{RT} \quad (\text{IV-8})$$

where n/V is the atomic density, P is the pressure, k is the Boltzmann constant, and T is the absolute temperature. This is just an approximation of the alkali number density since at these temperatures a small percentage of dimers, trimers, etc. will also be present

A wire was inserted slightly off center in the heat pipe to monitor ions or electrons during the experiment. A dc voltage was applied to the wire to collect ions or electrons. The ionization signal was observed as a voltage change due to the electronic flow through a 10k resistor to ground. The voltage was displayed on a oscilloscope, averaged by a boxcar integrator, and recorded on a x-y recorder.

Emissions from the heat pipe were directed into a scanning 1/3 meter monochromator (Instruments SA, Inc.) equipped with a visible blazed grating (800g/mm) or an infrared blazed grating (center wavelength 1100nm, 600g/mm) and recorded with a Hamamatsu (R928) photomultiplier tube which could be used out to 930nm. A Judson InAs photodiode was used to detect infrared radiation in the range from 0.8 μ m to 1.8 μ m. The voltage from either detector was displayed on a oscilloscope, averaged by a boxcar integrator, and recorded on a x-y recorder. The monochromator was calibrated with either line emissions from

the alkalis themselves or with Ne, Hg, and Kr lamps. In some cases, an optical multichannel analyzer (Princeton Applied Research, Inc., model 1205A) equipped with a photodiode array as a detector was used to analyze the output radiation.

Results and Discussion

Wave-mixing Processes

A number of non-linear optical processes were observed upon strong pumping of lithium, sodium, and potassium vapor at the two-photon resonance levels. A list of emissions from these processes are found in tables IV-1 - IV-3. Figure IV-4 shows the forward directed emissions when the focussed dye laser is tuned near the two-photon allowed $4d\ ^2D_{5/2,3/2}$ levels of sodium. Due to the bandwidth of the laser (0.2cm^{-1}) both of the $4d\ ^2D_{5/2,3/2}$ levels are excited.

The emissions in the region 785nm to 800nm consist of stimulated molecular emissions between the two lowest singlet molecular states of Na_2 . Setting the monochromator on one of the $1\ ^1\Sigma_u^+ \rightarrow 1\ ^1\Sigma_g^+$ emissions and scanning the dye laser shows that the $1\ ^1\Sigma_u^+$ state is populated via cascading transitions from excited states by one- or two-photon

Table IV-1. Observed emissions in lithium vapor.

EMISSION (Å)	TRANSITION	COMMENTS
<u>$2 \hbar\nu \rightarrow 3d \ ^2D$ ($\lambda_L = 6393\text{Å}$)</u>		
6104	$2p \ ^2P \rightarrow 3d \ ^2D$	
6708	$2s \ ^2S_{1/2} \rightarrow 2p \ ^2P$	
8126	$2p \ ^2P \rightarrow 3s \ ^2S_{1/2}$	
13201	?	"dip" on resonance

Table IV-2. Observed emissions in potassium vapor.

EMISSION (Å)	TRANSITION	COMMENTS
<u>$2 \hbar\nu \rightarrow 4d \ ^2D$ ($\lambda_L = 7300\text{Å}$)</u>		
4044	$4s \ ^2S_{1/2} \rightarrow 5p \ ^2P_{3/2}$	weak conical emission
4046	$4s \ ^2S_{1/2} \rightarrow 5p \ ^2P_{3/2}$	weak conical emission
4118	?	
4128	?	
<u>$2 \hbar\nu \rightarrow 5d \ ^2D$ ($\lambda_L = 6626\text{Å}$)</u>		
3446	$4s \ ^2S_{1/2} \rightarrow 6p$	
4044	$4s \ ^2S_{1/2} \rightarrow 5p \ ^2P_{3/2}$	
4118	?	
4128	?	
8080	?	only on resonance; weak
8085	?	only on resonance; weak
11500		occurs near resonance
12432	$4p \ ^2P_{1/2} \rightarrow 5s \ ^2S_{1/2}$	
12522	$4p \ ^2P_{3/2} \rightarrow 5s \ ^2S_{1/2}$	
<u>$2 \hbar\nu \rightarrow 6s \ ^2S$ ($\lambda_L = 7286\text{Å}$)</u>		
4044	$4s \ ^2S_{1/2} \rightarrow 5p \ ^2P_{3/2}$	strong conical emission
4046	$4s \ ^2S_{1/2} \rightarrow 5p \ ^2P_{1/2}$	strong conical emission
6911	$4p \ ^2P_{1/2} \rightarrow 6s \ ^2S_{1/2}$	weak
7699	$4s \ ^2S_{1/2} \rightarrow 4p \ ^2P_{1/2}$	weak
8080	?	only on resonance; weak
8085	?	only on resonance; weak
11690	$4p \ ^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	
11720	(see text)	axial phase matched; 6-WM
11773	$4p \ ^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	
12432	$4p \ ^2P_{1/2} \rightarrow 5s \ ^2S_{1/2}$	
12460	(see text)	axial phase matched; 6-WM
12522	$4p \ ^2P_{3/2} \rightarrow 5s \ ^2S_{1/2}$	
12802	(see text)	"special" 6-WM
13690	(see text)	"special" 6-WM

Table IV-2. (Continued)

EMISSIONS (Å)	TRANSITION	COMMENTS
<u>$2 \hbar\nu \rightarrow 7s \ ^2S$ ($\lambda_L = 6606\text{Å}$)</u>		
3446	$4s \ ^2S_{1/2} \rightarrow 6p \ ^2P_?$	
4044	$4s \ ^2S_{1/2} \rightarrow 5p \ ^2P_{3/2}$	strong conical emission
4046	$4s \ ^2S_{1/2} \rightarrow 5p \ ^2P_{1/2}$	strong conical emission
4118	?	
4128	?	
7698	$4s \ ^2S_{1/2} \rightarrow 4p \ ^2P_{1/2}$	weak
8080	?	only on resonance; weak
8085	?	only on resonance; weak
8108	(see text)	"special" 6-WM
8995	?	
11408	(see text)	"special" 6-WM
11773	$4p \ ^2S \rightarrow 3d \ ^2D$	
12432	$4p \ ^2S_{1/2} \rightarrow 5s \ ^2S_{1/2}$	
12522	$4p \ ^2S_{3/2} \rightarrow 5s \ ^2S_{1/2}$	
13368	$3d \ ^2D \rightarrow 6p \ ^2P$	

Table IV-3. Observed emissions in sodium vapor.

EMISSION (Å)	TRANSITION	COMMENTS
<u>$2 \hbar\nu \rightarrow 3d \ ^2D$ ($\lambda_L = 6856\text{Å}$)</u>		
5890	$3s \ ^2S_{1/2} \rightarrow 3p \ ^2P_{3/2}$	conical emission
5896	$3s \ ^2S_{1/2} \rightarrow 3p \ ^2P_{1/2}$	conical emission
8183	$3p \ ^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	
8195	$3p \ ^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	
<u>$2 \hbar\nu \rightarrow 4d \ ^2D$ ($\lambda_L = 5789\text{Å}$)</u>		
3065	?	
3082	?	
3302	$3s \ ^2S_{1/2} \rightarrow 4p \ ^2P$	
3325		
5596	?	"dip" on resonance
5610	?	"dip: on resonance"
8183	$3p \ ^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	
8195	$3p \ ^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	
8300	(see text)	"special" 6-WM
8400	(see text)	"special" 6-WM
<u>$2 \hbar\nu \rightarrow 5d \ ^2D$ ($\lambda_L = 5400\text{Å}$)</u>		
2853	$3s \ ^2S_{1/2} \rightarrow 5p \ ^2P$	
3203	?	
3253	?	
3302	$3s \ ^2S_{1/2} \rightarrow 4p \ ^2P_{3/2}$	
3303	$3s \ ^2S_{1/2} \rightarrow 4p \ ^2P_{1/2}$	
8183	$3p \ ^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	
8195	$3p \ ^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	
8557	?	similar to 8400 emission

Table IV-3. (continued)

EMISSION (Å)	TRANSITION	COMMENTS
<u>$2 \hbar\nu \rightarrow 6d \ ^2D$ ($\lambda_L = 5210\text{\AA}$)</u>		
2853	$3s \ ^2S_{1/2} \rightarrow 5p \ ^2P$	
3302	$3s \ ^2S_{1/2} \rightarrow 4p \ ^2P_{3/2}$	
8183	$3p \ ^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	
8195	$3p \ ^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	
<u>$2 \hbar\nu \rightarrow 4s \ ^2S$ ($\lambda_L = 7770\text{\AA}$)</u>		
2590	$3s \ ^2S_{1/2} \rightarrow 7p \ ^2P$	third harmonic light
5890	$3s \ ^2S_{1/2} \rightarrow 3p \ ^2P_{3/2}$	strong conical emission
5896	$3s \ ^2S_{1/2} \rightarrow 3p \ ^2P_{1/2}$	strong conical emission
<u>$2 \hbar\nu \rightarrow 7s \ ^2S$ ($\lambda_L = 5261\text{\AA}$)</u>		
2853	$3s \ ^2S_{1/2} \rightarrow 5p \ ^2P$	
3302	$3s \ ^2S_{1/2} \rightarrow 4p \ ^2P_{3/2}$	
<u>$3 \hbar\nu \rightarrow 7p \ ^2P$ ($\lambda_L = 7784\text{\AA}$)</u>		
2595	$3s \ ^2S_{1/2} \rightarrow 7p \ ^2P$	third harmonic light
<u>$3 \hbar\nu \rightarrow 6f \ ^2F$ ($\lambda_L = 7813\text{\AA}$)</u>		
2595	$3s \ ^2S_{1/2} \rightarrow 7p \ ^2P$	
5890	$3s \ ^2S_{1/2} \rightarrow 3p \ ^2P_{3/2}$	conical emission
5896	$3s \ ^2S_{1/2} \rightarrow 3p \ ^2P_{1/2}$	conical emission

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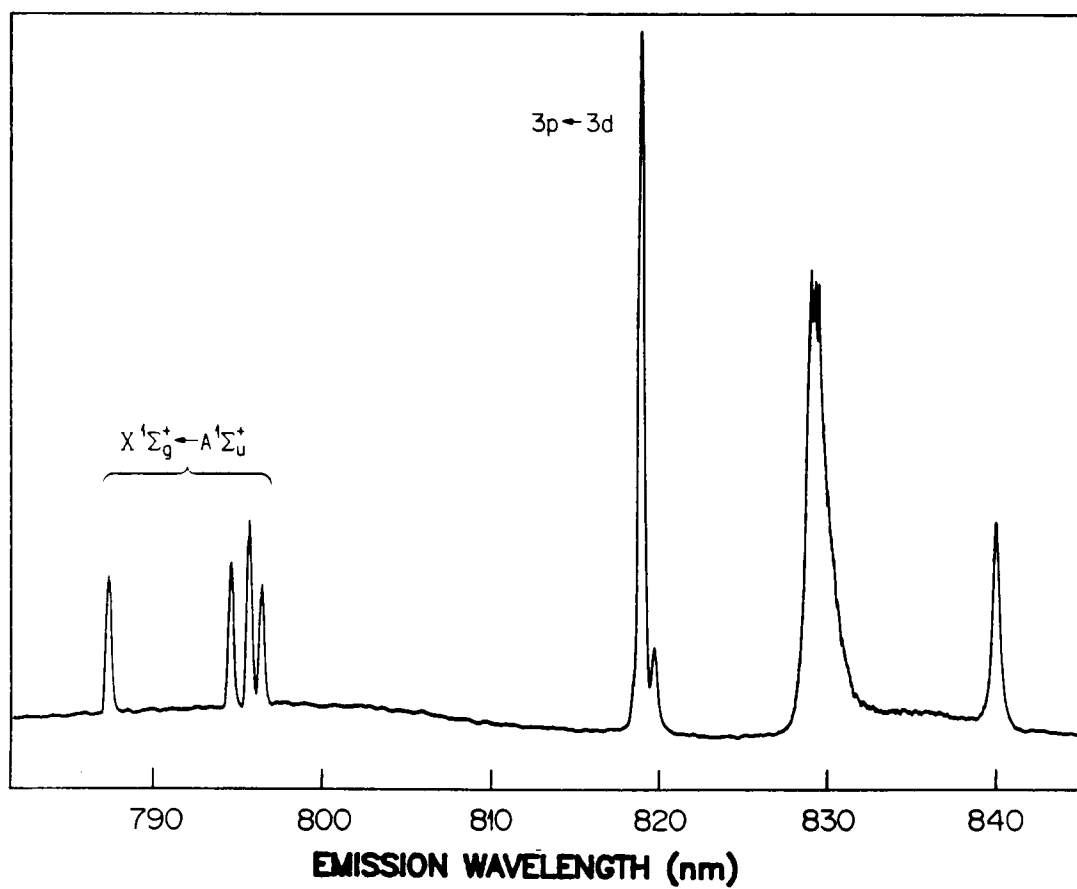


Figure IV-4. Forward-stimulated emissions when tuned near the two-photon allowed $4d\ ^2D_{5/2,3/2}$ levels in sodium. Sodium vapor pressure ~ 7 Torr.

excitation from the ground state vibrational levels. A clear ro-vibrational band separation is obtained in the excitation spectrum whose separation is found to be the 159 cm^{-1} vibrational spacing of the ground $1^1\Sigma_g^+$ state of Na_2 (figure IV-5).²⁰⁸ These molecular transitions have been studied extensively and will not be discussed here.^{190,209-211}

The features near 820nm correspond to stimulated electronic Raman scattering (SERS) from $3d\ ^2D_{5/2,3/2}$ levels to the $3p\ ^2P_{3/2,1/2}$ levels. This emission is a branch of the parametric six wave-mixing process

$$\omega_{3d-3p} = 2\omega_L - \omega_{4d-4p} - \omega_{4p-3d} - \omega_{3p-3s} . \quad (\text{IV-9})$$

While tuning near the $4d\ ^2D_{5/2,3/2}$ level in two-photons, two other emissions are also observed at ~830nm and ~840nm. These emissions do not correspond to any atomic transitions in sodium. Both have been found to be pressure dependent.

The emission at 840nm was originally assigned as a satellite of the 830nm emission which itself originally was assigned as emission from the lowest triplet levels ($1\ ^3\Sigma_u^+ - 1\ ^3\Sigma_g^+$) of Na_2 because of its breadth and apparent structure.²¹² Detailed studies of the 840nm emission show that it is forward directed and its frequency increases as the frequency of the dye laser decreases, the frequency of the emission corresponding to $\omega_{3d-3s} - \omega_L$.

Wang et al.²¹³ showed that the 830nm and 840nm emissions were not molecular in nature by performing an experiment in which a heating wire was inserted into the heat pipe close

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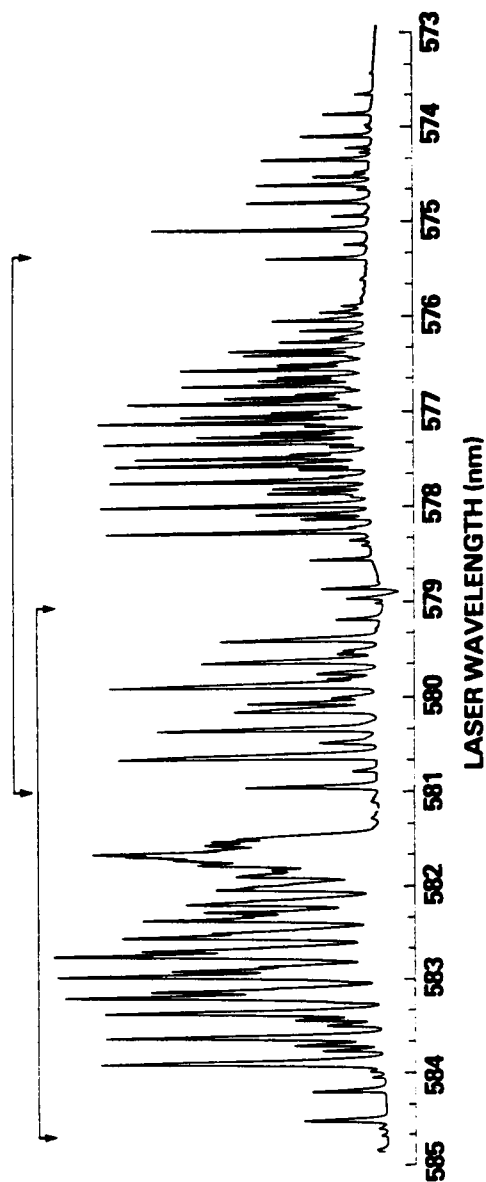


Figure IV-5. Stimulated singlet-singlet laser emissions between the $1\ \Sigma_u^+ \rightarrow 1\ 1\ \Sigma_g^+$ rovibrational levels. The separation of the bands, as indicated by the arrows, corresponds to the separation of the ground state, $1\ \Sigma_g^+$, vibrational levels ($\sim 159\text{cm}^{-1}$).

to the path of the light beam. The heating wire allowed for local superheating of the alkali vapor which resulted in thermal dissociation of dimers, trimers etc. This heated wire thus allowed for a strong reduction of the molecular concentration.²¹⁴ Upon heating, the molecular emissions ($1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$) completely disappeared. The 830nm and 840nm emissions on the other hand remained, indicating that they were atomic in nature.

From this fact, its directionality, and tuning behavior, it was determined that the 840nm emission was part of a special hyper-Raman six wave-mixing process involving a virtual state at the laser photon energy. Two-photon excitation of the $6s\ ^2S_{1/2}$ state of potassium produced similar emissions at 1.280 μ m and 1.369 μ m. All three of these emissions result from an anomalous dispersion in the alkali medium which, as a result of phase-matching conditions, generates these new waves. Similar studies involving this type of atomic parametric process were carried out earlier by Jackson and Wynne²¹⁵ using counterpropagating two-color experiments. From conservation of momentum these special hyper-Raman six wave-mixing processes can be represented as

$$\omega_{840nm} = 2\omega_L - \omega_{4d-4p} - \omega_{4p-3d} - \omega_L, \quad (IV-10)$$

$$\omega_{1.280\mu m} = 2\omega_L - \omega_{6s-5p} - \omega_{5p-3d} - \omega_L, \quad (IV-11)$$

and

$$\omega_{1.369\mu m} = 2\omega_L - \omega_{6s-5p} - \omega_{5p-5s} - \omega_L . \quad (IV-12)$$

The 830nm emission is also forward directed. While setting the monochromator at various points along the 830nm emission, the dye laser was scanned. A dramatic dip was noted in the resulting excitation spectrum of the 830nm emission occurring at the exact frequency of the two-photon resonant $3s \ ^2S_{1/2} \rightarrow 4d \ ^2D_{5/2,3/2}$ excitation (figure IV-6). The excitation of the $4d \ ^2D_{5/2,3/2}$ atoms can be monitored using the two-photon resonant ionization signal. At low pressures, the ionization signal is due to three-photon ionization, whereas at higher pressures chemi-ionization may also contribute. The measurement of the ionization signal is an approximate detector of $4d \ ^2D_{5/2,3/2}$ atoms. The strong three-photon, ac Stark broadened ionization signal is shown in figure IV-7 for low pressure. As the sodium pressure is increased, this ionization signal seems to decrease in magnitude. At higher pressures, the $4d \ ^2D_{5/2,3/2}$ ionization signal decreases until it is on the order of the molecular ionization signal (figure IV-8). All of the peaks in figure IV-8 are reproducible and are attributed to molecular resonant enhancement at the one-, two-, and three-photon level (autoionization). The "dip" in the 830nm emission appears to be associated with a decrease in the $4d \ ^2D_{5/2,3/2}$

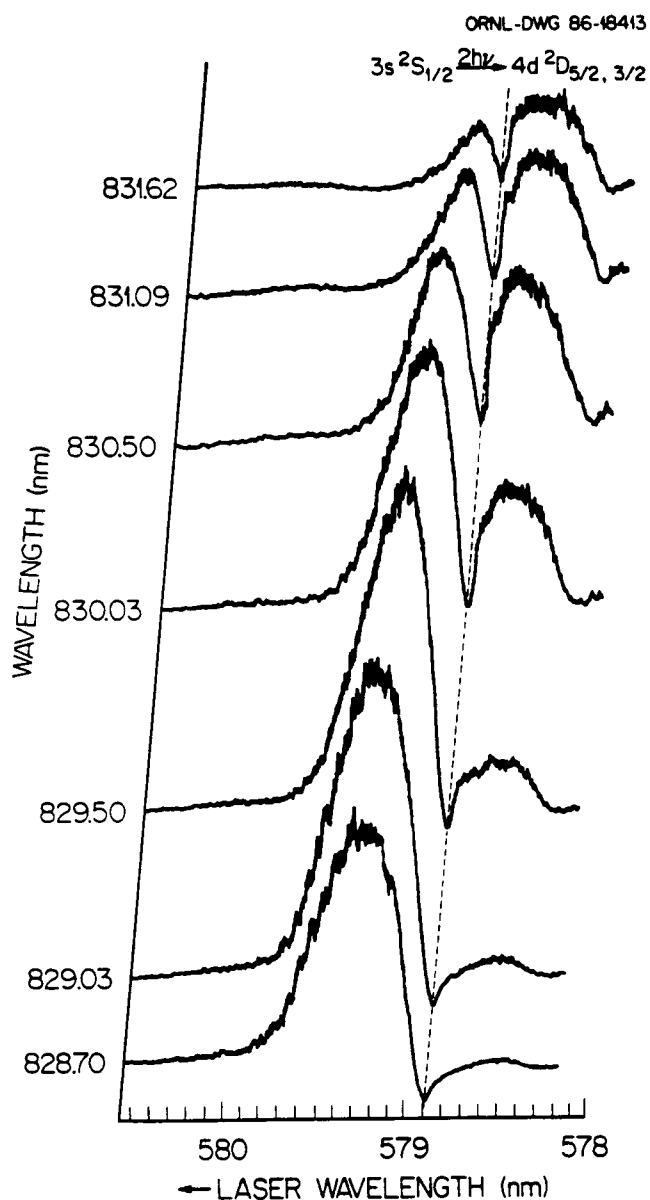


Figure IV-6. Excitation spectrum of 830nm emission. The observed "dip" occurs at the two-photon resonance to the $4d\ ^2D$ state.

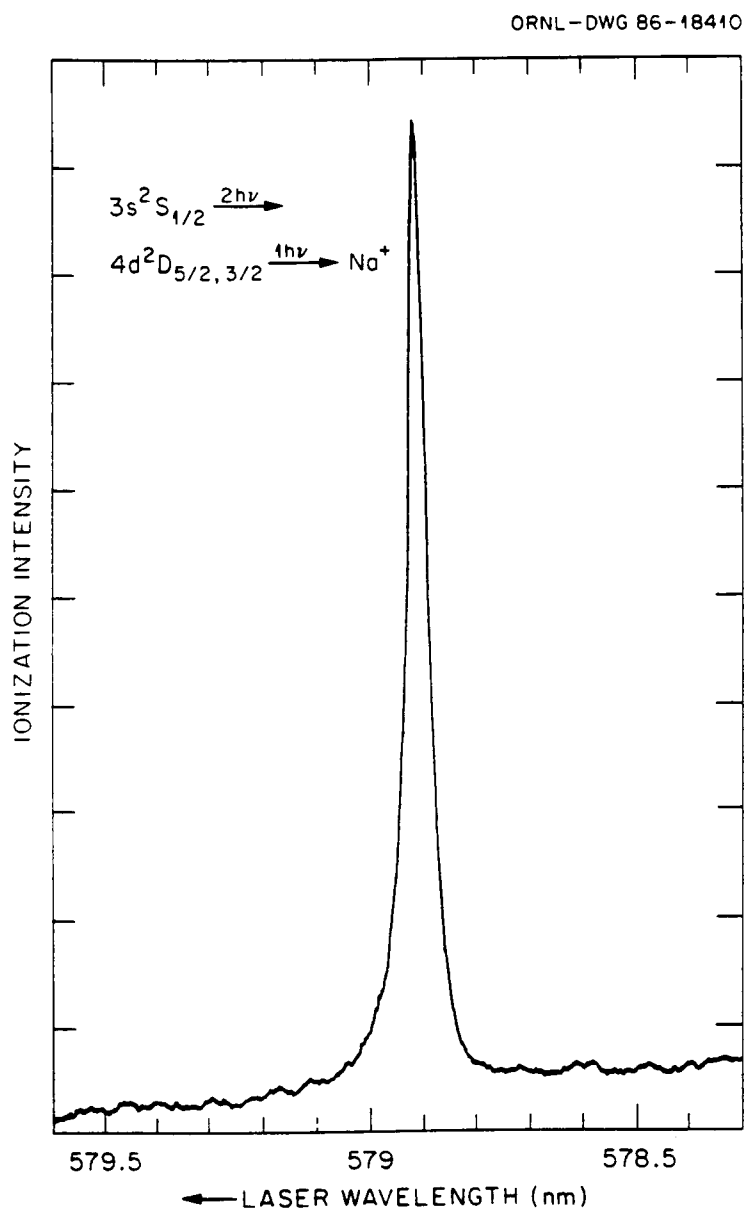


Figure IV-7. Resonantly enhanced (2+1) multiphoton ionization of sodium at low pressure (~0.8 Torr).

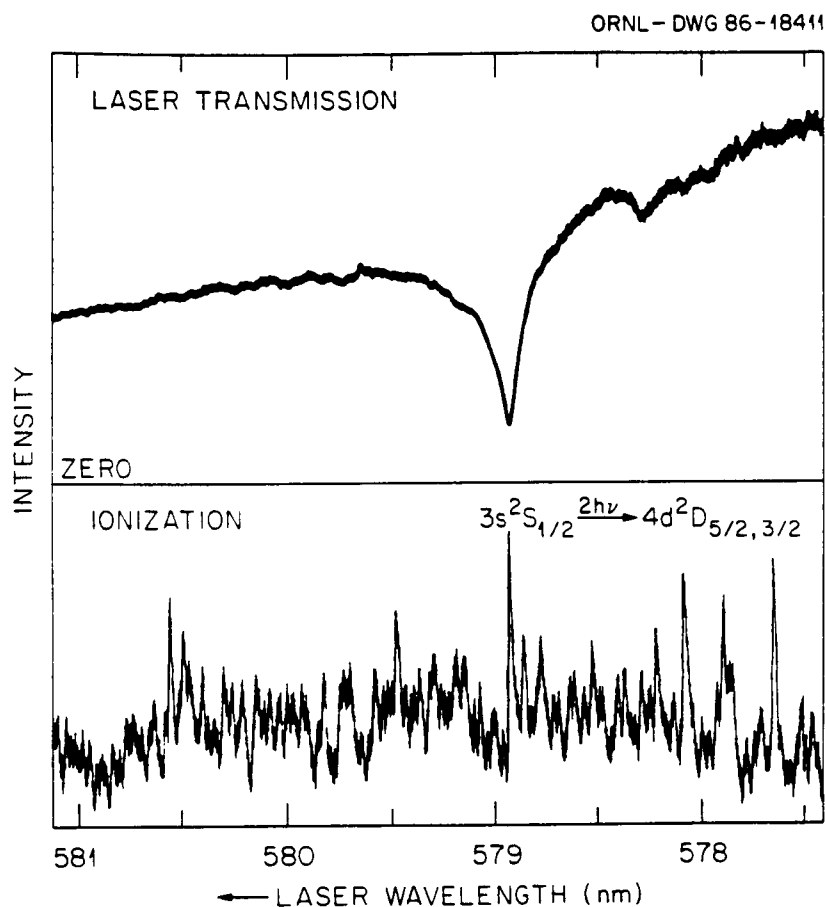


Figure IV-8. Resonantly enhanced (2+1) multiphoton ionization of sodium at high pressure (~7 Torr). The top portion of the figure shows the strong two-photon absorption of the incident laser light that occurs at the $4d\ ^2D$ resonance.

excitation. Note that there is a strong two-photon absorption as evidenced by the strong minimum of the transmitted laser light (figure IV-8). The strong two-photon absorption and suppression in ionization signal appear to be inconsistent. It is possible the strong SERS processes observed are also destructively interfering with the two-photon excitation process. This same interference effect was also observed in the two-photon excitation of the $3d\ ^2D_{5/2,3/2}$ levels in sodium. To the best of our knowledge this is the first observation of ionization suppression due to interference of the two-photon excitation.

Interference processes were first considered by Manykin and Afanas'ev²¹⁶ who calculated the suppression of two-photon absorption in two-photon resonantly enhanced third harmonic generation. While operating at pressures greater than one Torr, Aron and Johnson⁹¹ reported the absence of any multiphoton ionization signal while tuned to the three-photon allowed $6s[3/2]_1$ state of xenon. Compton et al.¹¹¹ later observed the ionization signal due to (3+2) MPI of xenon via the $6s[3/2]_1$ state while operating at low xenon pressures (<0.1 Torr). This was the first experimental implication that some sort of "cancellation" or interference mechanism can and was occurring in a multiphoton process.

Miller et al.⁹² in a further experiment, monitored both multiphoton ionization and third harmonic generated light from the $6s[3/2]_1$ state as a function of xenon pressure. It

was found that, as the third harmonic light grew in intensity, the magnitude of the multiphoton ionization signal would decrease. These results indicated that the generation of third harmonic light and the suppression of multiphoton ionization were somehow connected. Glownia and Sander²¹⁷ later confirmed Miller et al.⁹² results by restoring the MPI signal at higher pressures using circular-polarized counterpropagated beams in the excitation process. Generation of third harmonic light would be forbidden and therefore, the three-photon excitation would not be canceled. Jackson and Wynne⁹³ clearly demonstrated that the observed "cancellation" of the $6s[3/2]_1$ state in xenon was due to destructive interference between the generated third harmonic light and the three-photon excitation process. These authors reflected the linearly polarized beam back upon itself to restore the ionization signal. Under these conditions excitation occurs from absorption of two-photons from one beam and one-photon from the counterpropagated beam. Phase matching will not allow for third harmonic generation under these conditions.

Another example of interference involves the suppression of amplified spontaneous emission (ASE) by a four wave-mixing (FWM) process. This type of interference has been studied both experimentally and theoretically in sodium upon two-photon pumping at the $3d\ ^2D$ levels.^{218,219} Suppression occurs from competition of a second excitation

pathway created by the generation of new waves in the FWM process. Agarwal²²⁰ calculated that, under conditions when ASE is suppressed, the fields generated by the FWM process creates a squeezed state of the radiation field. Krasnikov et. al.²²¹ reported the suppression of the two-photon absorption for $3s \rightarrow 4s$ transition in sodium. Many additional experimental and theoretical studies have also examined this interference phenomena.²²²⁻²²⁶

Based on the above studies, the observation of suppression of the three-photon ionization signal and the "dip" in the excitation spectrum are deemed part of an interference process since strong two-photon absorption of the laser beam is occurring simultaneously.

Excluding the "dip" in figure IV-6, the 830nm emission exhibited similar tuning behavior as the 840nm emission. From its directionality and tuning behavior, it was believed to be part of a similar six wave-mixing process. Unfortunately, from its excitation profile and lack of observing any other emission to satisfy the phase matching condition while exciting the 4d levels, its origin remained a mystery. An analogous emission was searched for in potassium to help determine the origin of the 830nm emission in sodium. Upon two-photon excitation of the $7s \ ^2S_{1/2}$ state in potassium a number of emissions were observed (table IV-2). The emission at $1.1485\mu\text{m}$ was forward directed and mimicked the excitation profile of the 830nm emission in

sodium. An emission at 810.5nm was found also to be forward directed and its excitation profile exhibited the same breadth as that of the 1.1485 μ m emission although no "dip" was observed in the excitation profile. From conservation of energy and momentum these two emissions appear to be part of the same six wave-mixing process of the type

$$\omega_{1.1485\mu m} + \omega_{.8105\mu m} = 2\omega_L - \omega_{7s-5p} - \omega_{5p-5s} . \quad (IV-13)$$

Subsequently, from these results in potassium, a wave at 584nm was expected to be connected with the 830nm emission in sodium. Luh et al.²²⁷ studied the 830nm emission in sodium and in sodium-potassium mixtures. A wave was observed at 584nm that had the exact excitation profile as the 830nm emission. Luh et al. predicted and observed an analogous emission to that of the 830nm in a sodium-potassium mixture that was blue-shifted as a result of a change in the refractive index of the alkali-mixture vapor. The 830nm emission is assigned as part of the following six wave-mixing process

$$\omega_{830nm} + \omega_{584nm} = 2\omega_L - \omega_{4d-4p} - \omega_{4p-3d} . \quad (IV-14)$$

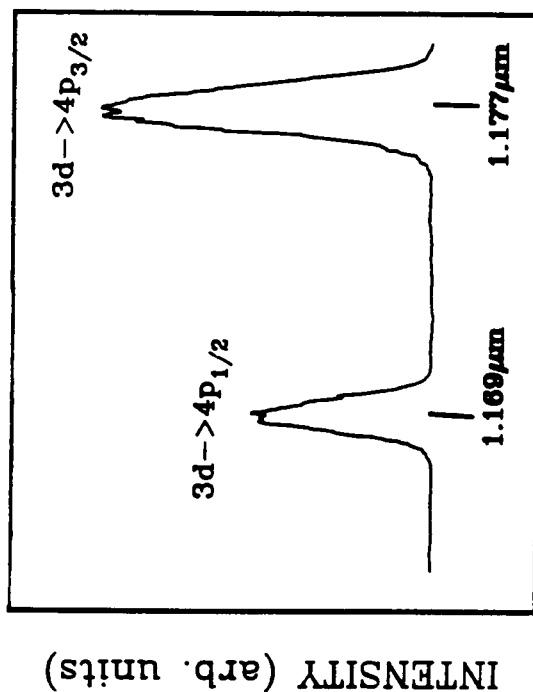
An interesting axial phase matched six wave-mixing process was observed upon two-photon excitation of the 6s $^2S_{1/2}$ state of potassium. At low potassium pressures, strong SERS and ASE signals were observed at 1.169 μ m and 1.177 μ m

corresponding to $3d\ ^2D_{5/2,3/2} \rightarrow 4p\ ^2P_{1/2}$ and $3d\ ^2D_{5/2,3/2} \rightarrow 4p\ ^2P_{3/2}$ transitions, respectively (figure IV-9). Strong SERS and ASE signals were also observed at $1.243\mu\text{m}$ and $1.252\mu\text{m}$ corresponding to $5s\ ^2S_{1/2} \rightarrow 4p\ ^2P_{1/2}$ and $5s\ ^2S_{1/2} \rightarrow 4p\ ^2P_{3/2}$ transitions, respectively (figure IV-10). As the pressure increased, two other emissions started to grow in at $1.172\mu\text{m}$ and $1.246\mu\text{m}$ between the fine structure states (figure IV-9 and 10). These new emissions are similar to the axially phased-matched parametric four wave-mixing emission observed recently in sodium by Moore et al.²²⁸ They arise from anomalous dispersion near the transition frequencies such that the phase matching condition is satisfied when the angle of propagation through the medium for the generated waves is zero. Since the nonlinear alkali vapor changes from being negatively dispersive to positively dispersive between the fine structure levels (see figure IV-3 for example), there is always a spot between them where axial phase matching may occur regardless of whether the exciting frequency is in a negative or positive dispersive region.

Hybrid Resonance

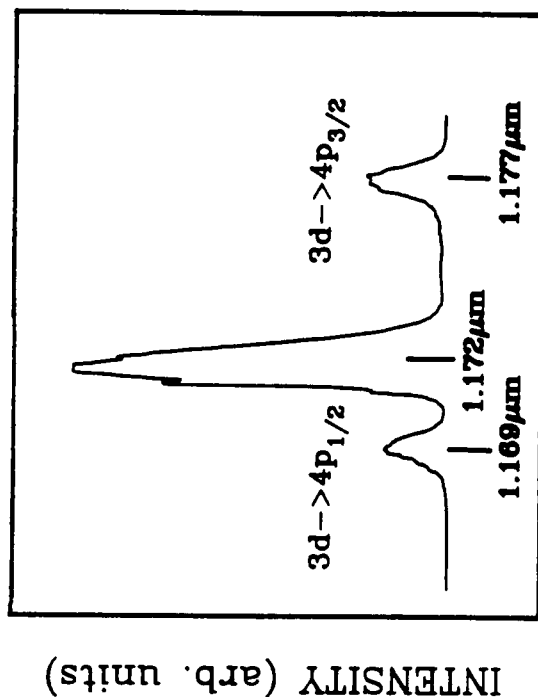
The stimulated emissions at 818.3nm and 819.7nm , in figure IV-4 were investigated as part of a parametric four wave-mixing process involving "hybrid resonances". Hybrid

POTASSIUM
LOW # DENSITY



Emission Wavelength

POTASSIUM
HIGH # DENSITY



Emission Wavelength

Figure IV-9. Forward-stimulated emissions from the 3d ²D_{5/2,3/2} levels when tuned near the two-photon allowed 6s ²S_{1/2} state in potassium at low (~1 Torr) and high pressure (~7 Torr). The emission between the atomic emissions is the result of an axially phase matched wave-mixing process.

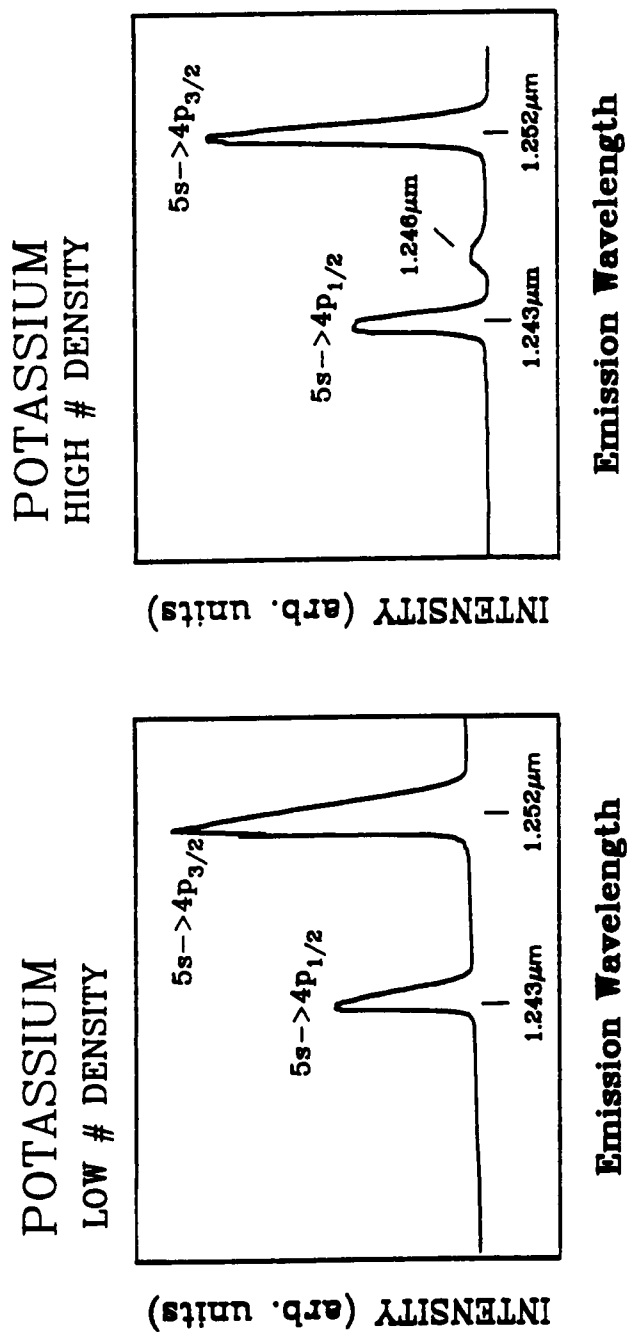


Figure IV-10. Forward-stimulated emissions from the $5s\ ^2S_{1/2}$ state when tuned near the two-photon allowed $6s\ ^2S_{1/2}$ state in potassium at low (~ 1 Torr) and pressure (~ 7 Torr). The emission between the atomic emissions is the result of an axially phase matched wave-mixing process.

resonances were first observed by Collins et al.²²⁹ while investigating the dissociation products of Cs_2 that resulted from the absorption of radiation from 620nm to 500nm. The ionization of atomic cesium was monitored while a dye laser was tuned through resonances that corresponded to transitions between excited intermediate states. Absorption of a photon from the dye laser excited the ground state Cs_2 molecule to a repulsive excited state of Cs_2 . The repulsive excited state immediately dissociates, resulting in the population of excited $5d\ ^2D_{5/2,3/2}$ and $6p\ ^2P_{3/2,1/2}$ cesium atoms. Absorption of two more photons from the excited states leads to ionization signals corresponding to $nf\ ^2F$ and $nd\ ^2D$ resonances, respectively.

The use of hybrid resonances furnished an alternative method of investigating high lying Rydberg states in atoms employing multiphoton ionization. Subsequent Rydberg studies, employing multiphoton ionization via hybrid resonances through the dissociation of molecules, have been conducted on rubidium,²³⁰ potassium,²³¹ indium,²³² yttrium,²³³ and gallium.²³⁴ Christian et al.²³⁵ have even measured the angular distribution of photoelectrons that resulted from hybrid resonances in cesium.

As the dye laser was tuned from 567nm to 570nm two strong ionization signals were observed (figure IV-11). The frequencies at which these ionization signals were observed correspond to two-photon resonant ionization via the $3p\ ^2P_{3/2}$

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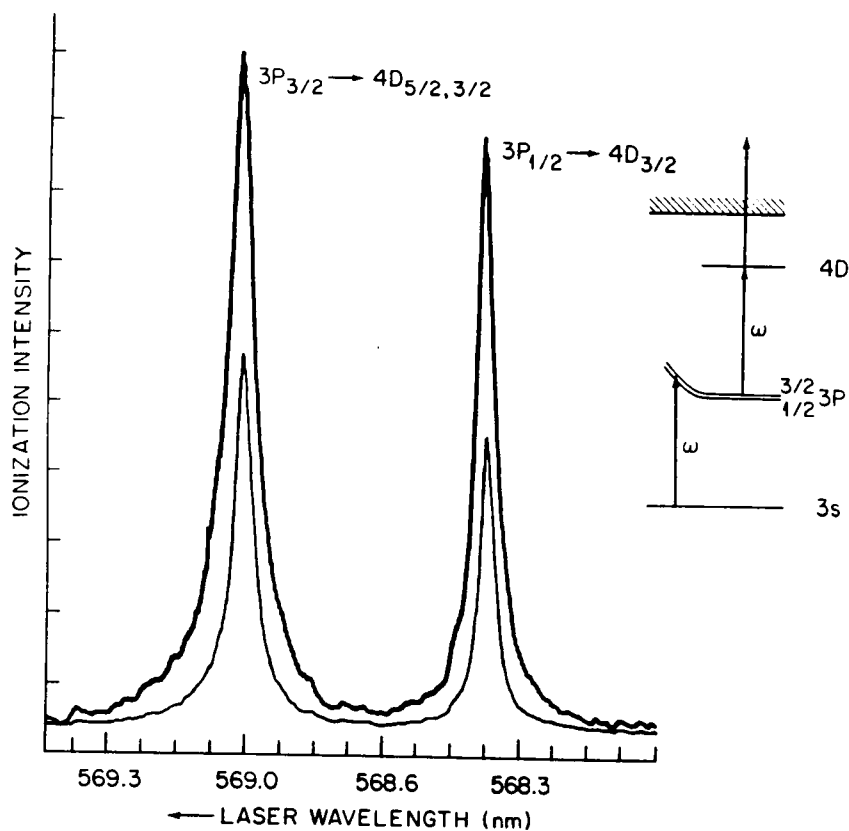
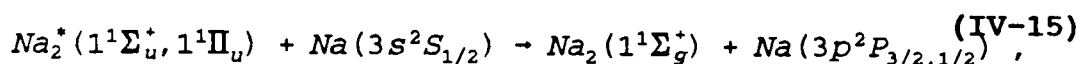


Figure IV-11. Two-photon ionization of sodium via hybrid resonances of the $3p\ ^2P_{1/2} \rightarrow 4d\ ^2D_{3/2}$ and $3p\ ^2P_{3/2} \rightarrow 4d\ ^2D_{5/2,3/2}$ atomic transitions. The inset shows that the $3p\ ^2P_{1/2,3/2}$ levels are populated through collisions between excited Na_2 molecules and ground state atoms.

$\rightarrow 4d\ ^2D_{5/2,3/2}$ and $3p\ ^2P_{1/2} \rightarrow 4d\ ^2D_{5/2,3/2}$ transitions in sodium. Population of the $3p\ ^2P_{3/2,1/2}$ levels is believed not to occur through the dissociation of Na_2 as in the above mentioned studies, but via a two-step process entailing excitation of bound Na_2 electronic states followed by collisional energy transfer (see inset in figure IV-11). The T_e values of the $1\ ^1\Sigma_u^+$ and $1\ ^1\Pi_u$ states of Na_2 are at $14680\ cm^{-1}$ and $20320\ m^{-1}$,²⁰⁸ respectively. The frequencies used to excite the $4d\ ^2D_{5/2,3/2}$ levels from the $3p\ ^2P_{3/2,1/2}$ levels are therefore sufficiently energetic enough to excite several high lying ro-vibrational levels of the $1\ ^1\Sigma_u^+$ state. Once excited, the Na_2^* molecules then collide with ground state Na atoms and subsequent energy transfer from the excited dimer to the atom occurs, populating the $3p\ ^2P_{3/2,1/2}$ levels. Collisional energy transfer of this type



has been studied extensively.^{236,237}

Intense stimulated electronic Raman signals were observed when the dye laser was tuned near the $3p\ ^2P_{3/2,1/2} \rightarrow 4d\ ^2D_{5/2,3/2}$ resonances. Similar intense SERS signals via hybrid resonances in sodium were first reported by Müller and Hertel²³⁸ exciting the $3p\ ^2P_{3/2,1/2} \rightarrow 5s\ ^2S_{1/2}$ transitions. They observed intense laser emissions at $3.415\ \mu m$ ($5s\ ^2S \rightarrow 3p\ ^2P_{3/2}$) and $3.408\ \mu m$ ($5s\ ^2S \rightarrow 3p\ ^2P_{1/2}$) when exciting either of the $3p\ ^2P_{3/2,1/2}$ levels.

In this study, exciting the $3p\ ^2P_{3/2}$ atoms to the $4d\ ^2D_{5/2,3/2}$ levels produced stimulated emission corresponding only to $3p\ ^2P_{3/2} \rightarrow 3d\ ^2D_{5/2,3/2}$ (819.5nm) whereas excitation of the $3p\ ^2P_{1/2}$ atoms to the $4d\ ^2D_{5/2,3/2}$ levels produced stimulated emissions corresponding mainly to $3p\ ^2P_{1/2} \rightarrow 3d\ ^2D_{5/2,3/2}$ (818.3nm) (figure IV-12). The slight emission at 819.5nm (corresponding to $3p\ ^2P_{3/2} \rightarrow 3d\ ^2D_{5/2,3/2}$) is probably due to competing ASE.

These stimulated emissions, from the $3d\ ^2D_{5/2,3/2}$ levels, are part of a four wave-mixing process of the type,

$$3p-4d-4p-3d-3p. \quad (IV-16)$$

Emissions from the $4p \rightarrow 4d$ and $3d \rightarrow 4p$ branches of the four wave mixing process are expected to occur at $2.3\mu\text{m}$ and $9.1\mu\text{m}$, respectively. The observation of these emissions was not possible because the detectors available did not extend out to these wavelengths. The $4p \rightarrow 4d$ transitions have been observed by Krökel et al.²¹⁴ using the same two-photon excitation scheme via a hybrid resonance. They did not report the observation of stimulated emission resulting from $3p\ ^2P_{3/2,1/2} \rightarrow 3d\ ^2D_{5/2,3/2}$ transitions.

Interestingly, emissions from the excited states involved in the four wave-mixing process, corresponding to transitions back to the ground state, were not observed. The only paths back to the ground state involve $3s\ ^2S_{1/2} \rightarrow 3p$

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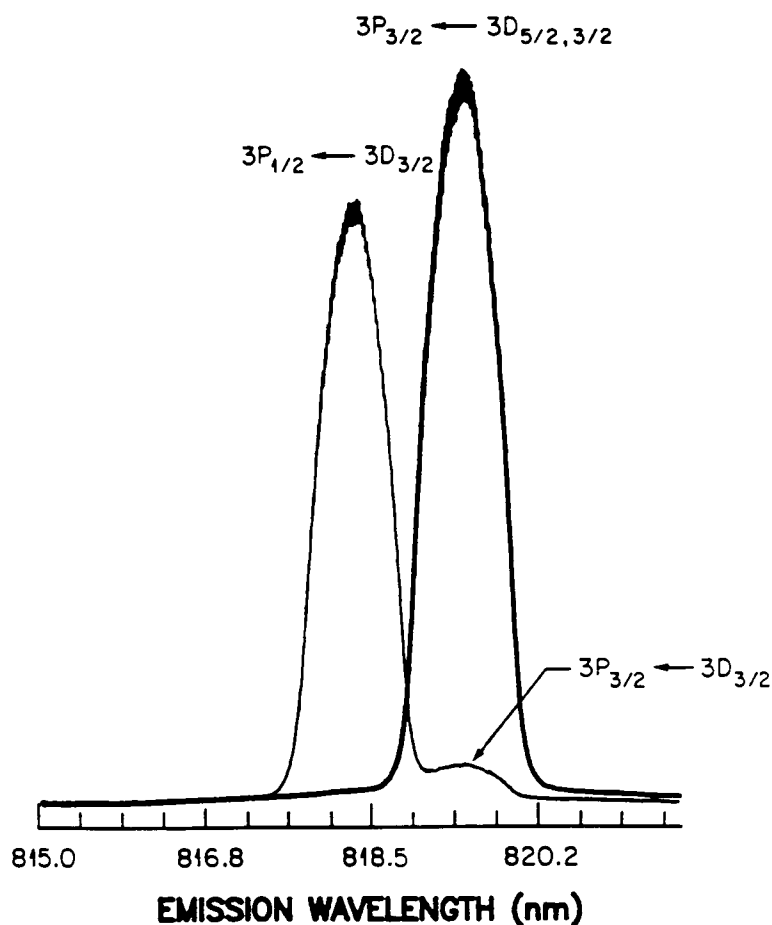


Figure IV-12. Stimulated electronic Raman signals in sodium corresponding to $3p\ ^2P \leftarrow 3d\ ^2D$ emissions via hybrid resonance excitation. Excitation of $3p\ ^2P_{1/2}$ atoms results in $3p\ ^2P_{3/2} \leftarrow 3d\ ^2D_{5/2,3/2}$ emission. Excitation of $3p\ ^2P_{3/2}$ atoms results in $3p\ ^2P_{1/2} \leftarrow 3d\ ^2D_{3/2}$ emissions.

$^2P_{3/2,1/2}$ (sodium D lines) and $3s\ ^2S_{1/2} - 4p\ ^2P_{3/2,1/2}$ transitions. A possible explanation for these missing emissions is that at this density they could be self absorbed since they are not parametricly connected.

The strong lasing between the $3p\ ^2P - 3d\ ^2D$ levels suggest this two-photon hybrid resonance is a potential source of strong infrared emission at 818.3nm and 819.5nm. Wang et al.^{209,239} have proposed a hybrid resonance laser and photodissociation laser based on analogous two-photon excitation schemes in potassium and sodium-potassium mixtures.

Conical Emission

Upon two-photon pumping some of the excited levels in sodium and potassium, an intense cone of light surrounding the laser beam was observed emerging from the heat pipe (see tables IV-2 and IV-3). For sodium, this cone or conical emission was an intense yellow color with its frequencies corresponding to that of the sodium D lines ($3s\ ^2S_{1/2} - 3p\ ^2P_{3/2,1/2}$). An intense blue cone was observed for potassium corresponding to $4s\ ^2S_{1/2} - 5p\ ^2P_{3/2,1/2}$ atomic transitions.

Conical emission was originally observed and studied as a SERS process in organic liquids such as benzene.²⁴⁰ The first observation of conical emission in an atomic vapor was reported by Grischkowsky.¹⁸⁷ Grischkowsky observed that,

when the output from a Raman-shifted ruby laser was tuned to the high frequency side of the $4s\ ^2S_{1/2} \rightarrow 4p\ ^2P_{1/2}$ transition in potassium, light corresponding to frequencies close to this transition was emitted as a diffuse ring around the self-focused laser beam. Since this early observation, conical emission has been observed and studied in barium,²⁴¹ strontium,²⁴² and sodium.²⁴³⁻²⁴⁷ The basic mechanisms of conical emission however are not fully understood.

Essentially two basic models have been proposed to explain conical emission. Golub et al.²⁴⁸ attributes the conical emission to a Cherenkov type process. Cherenkov radiation arises from an induced polarization in the alkali medium in which the phase velocity of the laser beam is greater than that of the emitted radiation which is emitted in the forward conical direction determined by $\cos\theta_c = v_{ph}/v$ where v_{ph} is the phase velocity of the emitted light.

The other model, which is more widely accepted, is based on an angle phased matched resonantly enhanced four wave-mixing process²⁴⁹ where the phase matching condition is expressed as

$$2k_1\cos\theta_1 = k_2\cos\theta_2 + k_3\cos\theta_3 . \quad (IV-17)$$

The $\cos\theta$ factor is added to account for modification of the phase matching angle conditions due to self focusing effects.²⁴⁹

Comparison of the two models, for a one-photon resonant

conical emission process, shows that the parametric four wave-mixing model predicts a cone angle that is a factor of $\sqrt{2}$ to 2 smaller than that of the actually measured cone angle. The Cherenkov radiation model, on the other hand, accurately predicts the cone angle for a one-photon resonant process.²⁴⁷ The factor of $\sqrt{2}$ to 2 results from self focussing of the laser beam which usually occurs along with the conical emission process. Self focussing of the laser beam leads to saturation effects in the change of the refractive index at the self-trapped filament surface where conical emission originates, severely influencing the emission angle. In a two-photon resonant process, under conditions that avoid self focussing effects, the four wave-mixing model has been found to adequately describe the two-photon resonant conical emission processes.²⁴⁵

In this study, we have determined the angle of the conical emission while exciting the $4s\ ^2S_{1/2}$ state of sodium in two-photons. The atomic number density of the sodium vapor at 1 Torr was estimated to be approximately 3.6×10^{16} atoms/cm³. Figure IV-13 shows the intensity of the two sodium D lines as a function of the distance from the laser beam axis. As can be seen from this data, there were actually two cones present containing both D line

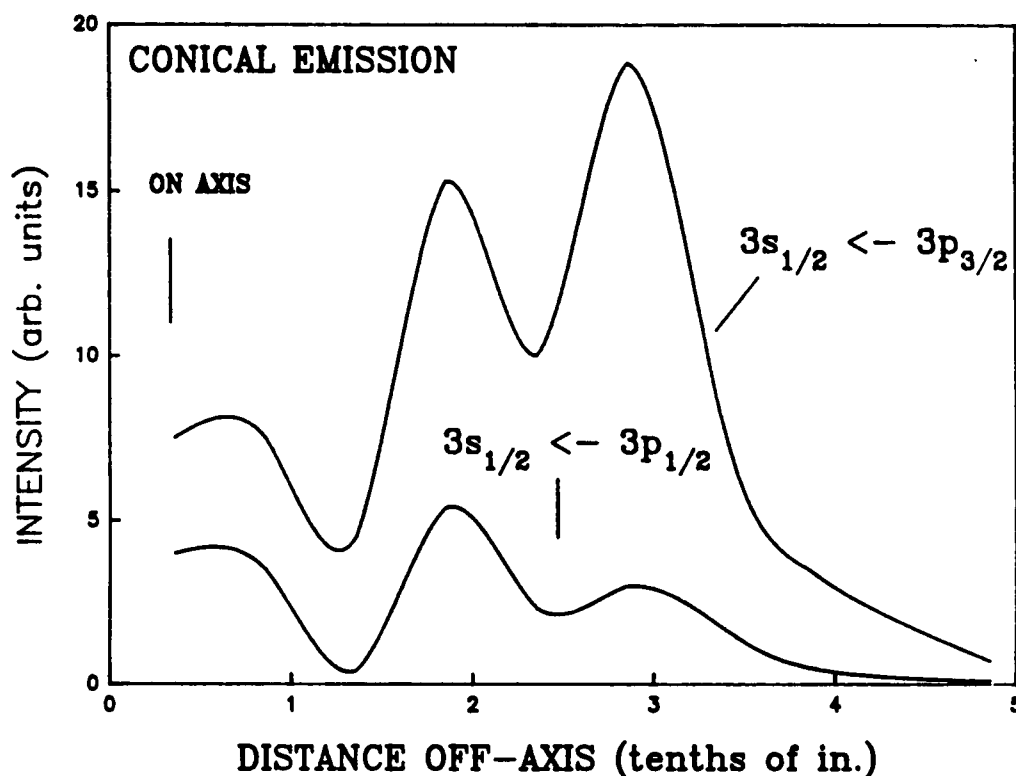


Figure IV-13. Measurement of conical emission that occurs when tuned near the two-photon allowed $4s\ ^2S_{1/2}$ state in sodium. The bottom trace corresponds to $3s\ ^2S_{1/2} \leftarrow 3p\ ^2P_{1/2}$ emissions and the top trace corresponds to $3s\ ^2S_{1/2} \leftarrow 3p\ ^2P_{3/2}$ emissions. Note that these two emissions also are observed on axis. These on axis emissions correspond to amplified spontaneous emission. $P_{Na} \sim 1$ Torr.

components. These measurements were taken with the dye laser slightly tuned off resonance ($\Delta\lambda \approx 0.15\text{\AA}$). Measuring the cone angle as a function of laser detuning was not quantitatively done. Qualitatively, the cone angle became larger as the laser was tuned closer to the atomic resonance. Conical emission was observed with the dye laser detuned up to $5\text{\AA}$ from line center.

The angle of the inner cone, based on these measurements, was estimated to be ~ 157 millirads and that of the outer cone to be ~ 242 millirads. The angle of the inner cone agrees quite well with that predicted by the angle phased match four wave-mixing model.²⁴⁵

The inner cone angle was calculated using the model described by Krasinski et al.²⁴⁵ Figure IV-14 shows the wavevector diagram depicting the conical emission process. ω_1 represents the two laser photons exciting the $4s\ ^2S_{1/2}$ state, ω_2 represents the stimulated emission from the $4s\ ^2S_{1/2}$ state to the $3p\ ^2P_{1/2,3/2}$ levels. θ_2 represents the angle at which the $3p\ ^2P_{1/2,3/2} \leftarrow 4s\ ^2S_{1/2}$ light is emitted and θ_3 represents the angle at which the sodium D lines are emitted at. The angle, θ_3 , was calculated by solving the following equation

$$\theta_3^2 = \frac{(\eta_3 + 1) + (\omega_1/\omega_3)\theta_1^2}{\eta_3(1 + \eta_3\omega_3/\omega_2)/2}, \quad (\text{IV-18})$$

where $\eta_3 = 1 + (1.4 \times 10^{-19})N/\Delta\lambda$ with N in cm^{-3} and $\Delta\lambda$ in

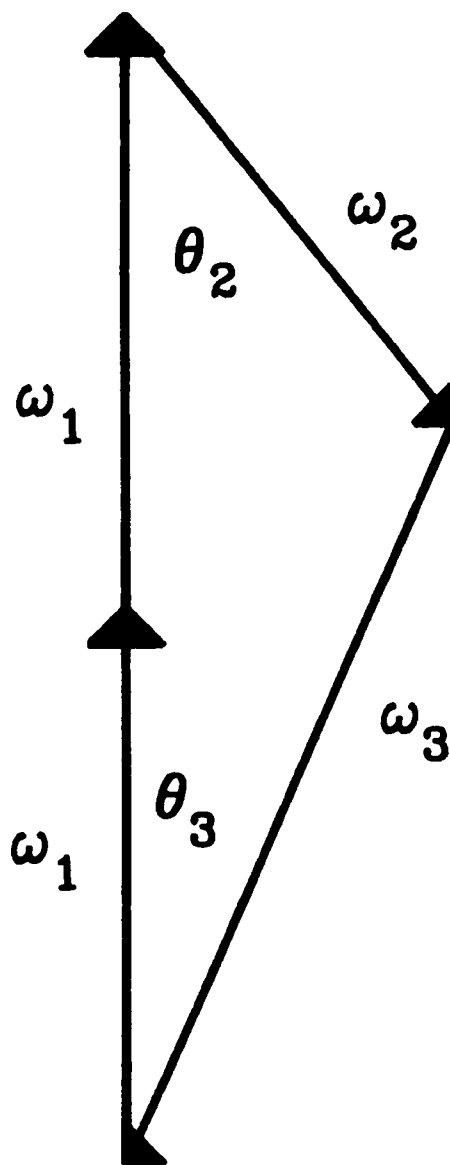


Figure IV-14. Wavevector diagram depicting four wave-mixing conical emission.

angstroms. ω_1 corresponds to the exciting frequency of the laser, ω_2 corresponds to the frequency of the $3p\ ^2P - 4s\ ^2S$ transition, and ω_3 corresponds to the frequency of the $3s\ ^2S - 3p\ ^2P$ transition. In this experiment N was estimated to be approximately 3.6×10^{16} sodium atoms/cm³.

If we take ω_3/ω_2 to be 1.93, equation IV-18 reduces to

$$\theta_3^2 = \frac{0.005/\Delta\lambda}{(1 + 0.005/\Delta\lambda)(1.465 + 0.005/\Delta\lambda)}, \quad (\text{IV-19})$$

where $\Delta\lambda$ represents the laser detuning from the two-photon resonance. Figure IV-15 shows the calculated change in cone angle as a function of laser detuning. For a detuning of $0.15\text{\AA}$, the inner cone angle was extrapolated to be ~ 147 mrad. This is in excellent agreement with the experimentally measured value of ~ 157 mrad.

The origin of the second cone is probably the result of a competing wave-mixing process. This competing wave-mixing process could possibly involve the $7p$ level since the absorption of another photon lies near the $7p\ ^2P_{3/2,1/2}$ levels. One possible wave-mixing process could involve a vacuum ultraviolet (VUV) photon since third harmonic generation is possible at this frequency. A possible four wave-mixing process, involving a VUV photon, would be

$$\omega_{\text{cone}} = \omega_{\text{VUV}} - \omega_{7p-nd, ns} - \omega_{nd, ns-3p} \quad (n = 4, 5, 6), \quad (\text{IV-20})$$

This type of wave-mixing process is plausible as evidenced by the fact that conical emission was also observed when exciting the $6f$ state. It is also found that exciting the

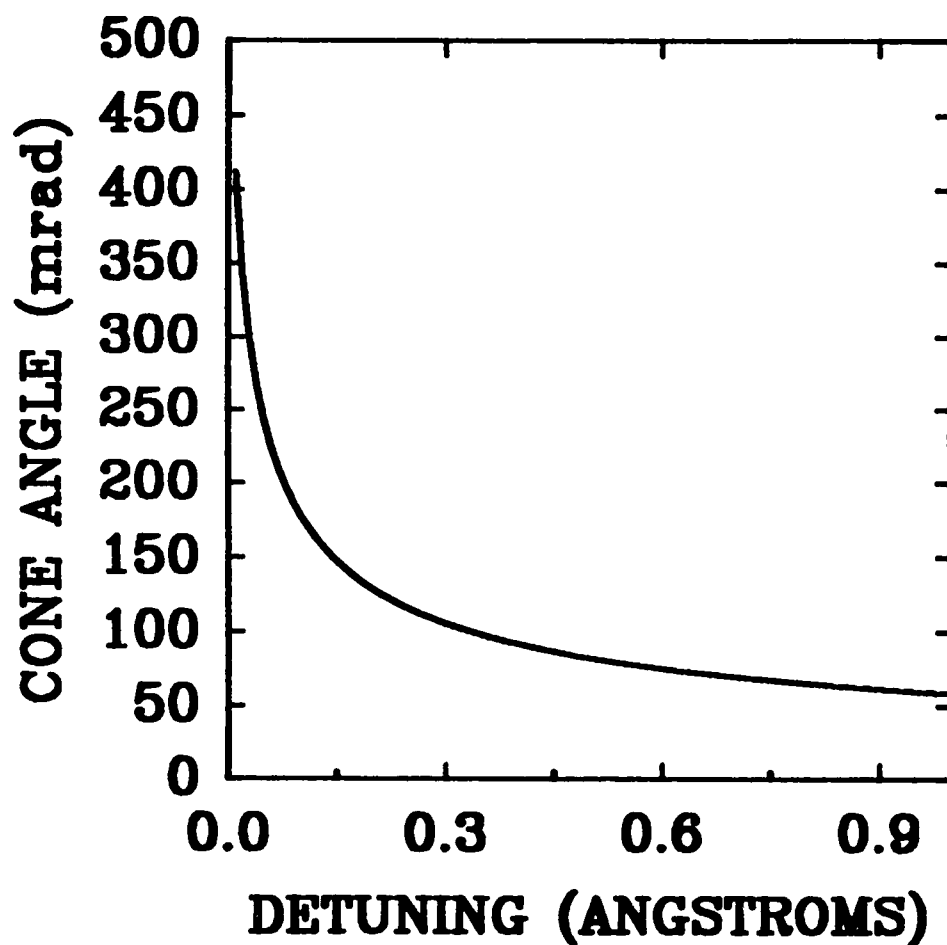


Figure IV-15. Calculated cone angle of $3s\ ^2S_{1/2} \rightarrow 3p\ ^2P_{1/2,3/2}$ versus laser detuning from two-photon resonance with the $4s\ ^2S_{1/2}$ state of sodium. Sodium pressure approximately 1 Torr.

6f state results in a VUV photon corresponding to the energy of the 7p level (see section on third harmonic generation in sodium).

Although not studied in detail, it should be noted that emissions corresponding to the sodium D lines were also observed when tuning near the $3p\ ^2P_{1/2}$ and $3p\ ^2P_{3/2}$ levels in one-photon. The emission from the heat pipe was not conical, as described above. In fact, no on axis emissions were observed, including the laser beam. What was emitted appeared to be spots of light flickering on and off at all different angles. These emissions were the result of "self-trapped filaments." Self-trapped filaments arise from severe self-focusing in the nonlinear medium resulting in saturation of the nonlinear index. Self-focusing of the light pulse from the dye laser produces two focal points. The positions of these foci change with time with the leading focal point moving in the forward direction and the trailing focal point moving backward toward the front of the heatpipe. These moving foci appear as filaments of light in the medium.

The sodium pressure in this particular study was seven Torr. Since the $3s\ ^2S_{1/2} - 3p\ ^2P_{1/2}$ and $3s\ ^2S_{1/2} - 3p\ ^2P_{3/2}$ transitions contain approximately 98% of the total oscillator strength, a dramatic change in the refractive index will occur as the exciting frequency nears these resonances. At this number density, severe "self-focussing"

effects will occur, making the laser beam appear to break up into intense streaks or filaments of light. An indepth treatment of self-focussing and filaments of light has been presented by Loy and Shen.²⁵⁰

Third Harmonic Generation in Sodium Vapor

A special type of four wave-mixing is known as third harmonic generation. Third harmonic generation in gases was first reported by Ward and New.²⁹ They measured third harmonic generation of a Q-switched ruby laser in a number of gases. These gases included air, chlorine, ethylene, oxygen, nitrogen, carbon dioxide, hydrogen, krypton, xenon, argon, and helium. In addition, they also presented theoretical calculations of the third order nonlinear susceptibility of these gases.

Harris and Miles^{251,252} showed that third harmonic generation, in alkali metal vapors, can have significantly larger conversion efficiencies if the focussed laser beam has a frequency below the atomic transition. The generated third harmonic frequency will then be negatively dispersive creating a phase mis-match, where $\eta_{(3\omega)} < \eta_{(\omega)}$. To compensate for the phase mis-match, which arises from the dispersion of the refractive indices between the incident frequency and third harmonic frequency, a positive dispersive buffer gas can be added to vary the refractive index until both the

incident frequency and third harmonic frequency are travelling at the same phase velocity. Bjorklund²⁵³ has provided a rigorous analysis of phase matching conditions of various third order processes under focussed conditions.

Bloom et al.³⁰, Hodgson et al.²⁵⁴, and Leung et al.²⁵⁵ demonstrated that the conversion efficiencies can further be increased by taking advantage of two-photon resonances in the alkali vapor. Hodgson et al.²⁵⁴ brought in a second laser at a tunable frequency, ω_2 , to develop a tunable vacuum ultraviolet light source ($2\omega_1 + \omega_2$), exploiting the two-photon resonance.

In this study, generation of third harmonic light in sodium vapor was investigated at low number densities while tuning near the $7p\ ^2P_{3/2,1/2}$ fine structure levels. The separation of the fine structure state is 0.71 cm^{-1} . Since the bandwidth of the laser was estimated to be $>0.5\text{ cm}^{-1}$, selective excitation of the fine structure states was not possible. The apparatus used to simultaneously study multiphoton ionization and third harmonic generation in sodium vapor is the same as described previously.

Output from the dye laser was loosely focused into the heat pipe containing sodium and argon with a 300mm focal length lens and tuned near the three-photon resonance of the $7p\ ^2P_{3/2,1/2}$ fine structure levels. The second photon in this excitation process is nearly resonant with the two-photon allowed $4s\ ^2S_{1/2}$ state. Energetically, the second photon

lies approximately 50 cm^{-1} below the $4s \text{ } ^2S_{1/2}$ state (see figure IV-16a). Thus, in this excitation scheme a two-fold enhancement is expected for third harmonic generation. This two-fold enhancement may be easily understood by examining the third order non-linear susceptibility which describes third harmonic generation. The third order non-linear susceptibility for third harmonic generation may be expressed as

$$\chi^{(3)}(-\omega_2, \omega_L, \omega_L, \omega_1) = \frac{(ea_0)^4}{(\hbar c)^3} \sum_{ijk} \frac{\mu_{gi}\mu_{ij}\mu_{jk}\mu_{kg}}{(\Omega_i - \omega_L)(\Omega_j - \omega_{2L})(\Omega_k - \omega_{3L})}, \quad (\text{IV-21})$$

where μ_{jk} is the electric dipole matrix element between levels j and k , g denotes the ground state, a_0 is the atomic Bohr radius, and $\Omega_i = (E_i - E_g)/\hbar - i\Gamma_i$.

When the input frequency is such that twice or thrice its magnitude is degenerate with an allowed transition, the second and third terms in the denominator of equation IV-21 approach zero, thereby increasing the magnitude of $\chi^{(3)}$.

The degree of enhancement that can be obtained will depend on the amount of absorption of the laser beam. For a two-photon resonant process, absorption of the third harmonic beam is very weak. As a result, much larger enhancements are expected for two-photon resonant processes than for three-photon near resonant processes where the third harmonic beam can undergo absorption. Two-photon resonant third harmonic generation in metal vapors was first

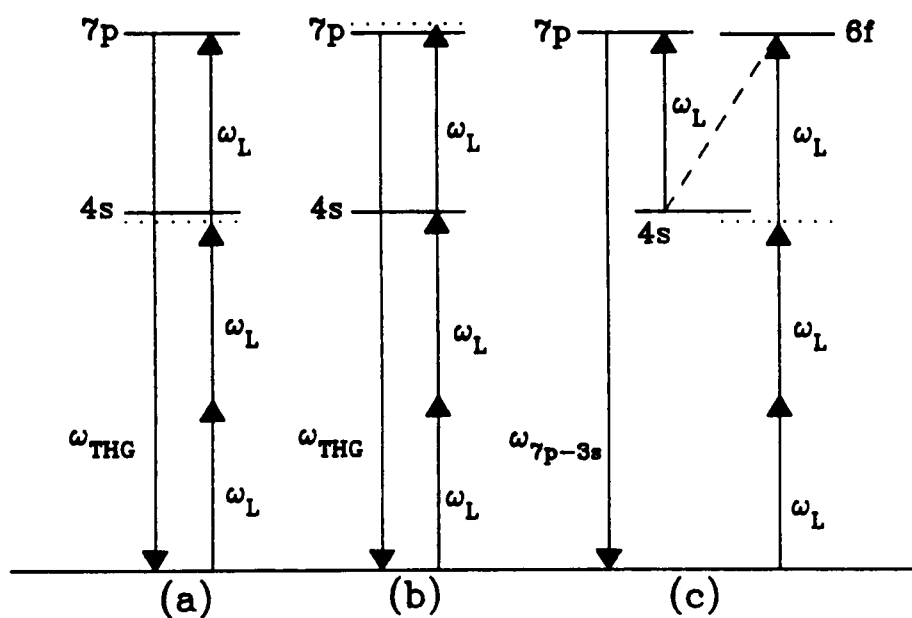


Figure IV-16. Schematic diagram depicting various paths studied in the generation of ultraviolet light from the 7p 2P state in sodium.

reported by Bloom et al.³⁰, Hodgson et al.²⁵⁴, and Leung et al.²⁵⁵

To the best of our knowledge, the studies reported herein represent the first three-photon resonantly enhanced third harmonic generation in an alkali vapor. Tuning near the $7p\ ^2P_{3/2,1/2}$ fine structure levels in sodium produced radiation which corresponded to three times the input frequency ($\sim 2595\text{\AA}$). This radiation was observed at sodium pressures of one Torr or less. The radiation was forward directed and emitted colinearly with the laser beam. The light was analyzed by being dispersed in a 1/3 meter monochromator (ISA, Inc) with a grating blazed in the visible and detected with a Hamamatsu (R928) photomultiplier tube. The intensity of the third harmonic light was low compared to background emissions. Two possible reasons for the low conversion efficiency observed in this experiment could involve apparatus considerations. First, the grating used in dispersing the radiation, although blazed for the visible, may not be able to handle the UV generated radiation. Second, the response of the photomultiplier at this particular frequency is not as high as it is in the visible region. A third possible reason for this apparent low conversion efficiency, although not investigated, could involve phase matching considerations.

In third harmonic generation, the intensity of the generated UV light is expected to vary as the cube of the

laser power. Examination of the third harmonic light as a function of laser power showed a quadratic dependence. This type of dependence is indicative of two-photon resonant third harmonic generation. The second photon in this process is probably ac Stark shifted into resonance and hence accounts for the observed dependence.

Absorption of another photon from the $7p\ ^2P_{3/2,1/2}$ levels leads to ionization. At pressures less than 1 Torr, strong ionization signals, corresponding to three-photon resonant, four-photon ionization from the $7p\ ^2P_{3/2,1/2}$ levels was observed. At pressures greater than one Torr, no multiphoton ionization signals were observed. Also at these pressures, no third harmonic light was observed. The disappearance of the multiphoton ionization signal and disappearance of the third harmonic light suggests that some type of interference process may be occurring. Interference of third harmonic light and three-photon excitation processes have been extensively studied for three-photon excitation of the $6s[3/2]_1$ state of xenon.^{92,93,217}

An attempt was made to disrupt any cancellation process that may have been occurring by retro-reflecting the laser beam back through the heat pipe. Absorption of two photons from one beam followed by the absorption of another photon from the other beam leads to excitation of the $7p\ ^2P_{3/2,1/2}$ levels. Since momentum cannot be conserved in this type of excitation scheme (i. e. third harmonic light will not be

generated), the absorption of another photon from either beam is expected to restore the ionization. No ionization signals were observed in the retro-reflection experiment. The absence of the multiphoton ionization signal, upon retro-reflection, is not understood at this time. Further experiments will be required to unravel this intriguing puzzle.

Tuning the dye laser toward higher energies, radiation corresponding to third harmonic light was observed when the second photon was coincident with the $4s\ ^2S_{1/2}$ state at low pressures. The third-photon in this excitation process lies approximately 70 cm^{-1} above the $7p\ ^2P_{3/2,1/2}$ fine structure levels (see figure IV-16b). A two-fold enhancement in third harmonic generation is also expected at this excitation frequency: resonant enhancement at the two-photon level and near-resonant enhancement at the three-photon level. The measured frequency of the third harmonic light was three times the frequency of the dye laser. The frequency of the third harmonic light corresponded to a wavelength of $\sim 2590\text{\AA}$. In addition to third harmonic light, strong conical emission was observed in the forward direction while exciting at this frequency. The measured frequencies of the conical emission corresponded to $3s\ ^2S_{1/2} \rightarrow 3p\ ^2P_{3/2,1/2}$ transitions. The conical emission is part of a competing four wave-mixing process. A discussion of this conical emission is presented above.

Strong MPI signals and conical emission were observed up to 10 Torr when the dye laser was tuned near two-photon resonance with the $4s\ ^2S_{1/2}$ state. Curiously, third harmonic light disappeared at pressures greater than one Torr. Study of the third harmonic light as a function of laser power at this frequency exhibited an approximately linear dependence. This type of linear dependence suggests that the excitation process is saturated probably because of the resonant enhancement at the second photon level. Saturation effects in two-photon resonant third harmonic generation have been studied in thallium²⁵⁶ and cesium.²⁵⁷

The excitation spectrum of the third harmonic radiation is shown in figure IV-17. The excitation spectrum was taken by setting the monochromator at 2595Å and then scanning the dye laser. Radiation (~2595Å) which corresponded to emission from the $7p\ ^2P_{1/2,3/2}$ levels was observed when the frequency of the dye laser was coincident with three-photon excitation of the 6f state. Although an f-s transition is not allowed in a single photon, it turns out that the frequency needed to excite the 6f in three-photons corresponds to the same frequency needed to excite the 7p state in a single photon from the 4s state (figure IV-16c). Resonant enhancement between excited states in a four wave-mixing process has been observed previously.^{258,259} How the 4s state is populated is unknown but believed to involve a wave-mixing process as evidenced by the weak conical

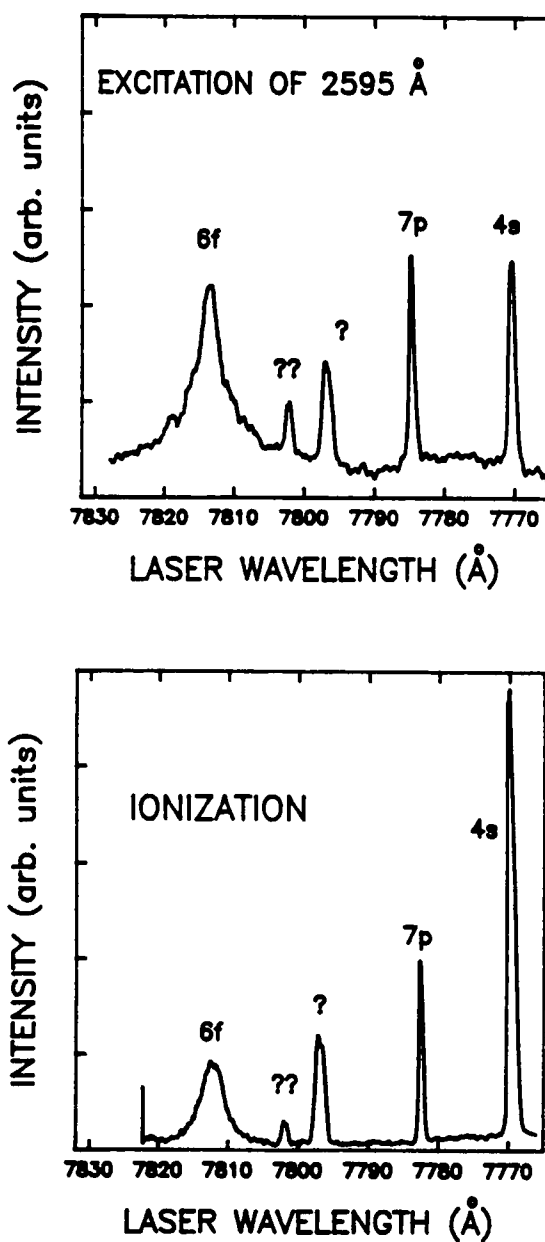


Figure IV-17. Excitation spectrum of 2595Å emission and MPI spectrum while tuning near the three-photon allowed 7p 2P state in sodium. Sodium pressure ~1 Torr.

emission that is observed in the forward direction at pressures greater than 1 Torr. Radiation corresponding to $3s\ ^2S_{1/2} - 3p\ ^2P_{3/2,1/2}$ transitions was observed in the backward direction. Radiation in the backward direction is indicative of amplified spontaneous emission. The radiation observed at $\sim 2595\text{\AA}$ when the dye laser frequency corresponds to three-photon excitation of the $6f$ state, is not due to third harmonic generation but due to a wave-mixing process or a cascading process due to population inversion.

Two other resonances were also observed in the excitation spectrum of third harmonic light. These two resonances are labeled ? and ?? in figure IV-17 and occur at $\omega_{?} \approx 12825\text{cm}^{-1}$ and $\omega_{??} \approx 12816\text{cm}^{-1}$. The emission from the signal labeled ? is centered at $\sim 2592\text{\AA}$ when the dye laser is tuned to its resonance. An ionization spectrum, taken at the same pressure as the excitation spectrum, show these same two resonances occurring at the same excitation frequencies as in the excitation spectrum (figure IV-17). The excitation frequencies at which these two signals are observed do not correspond to any one-, two-, or three-photon atomic transitions in sodium. At pressures greater than one Torr, both the UV radiation and multiphoton ionization signal at these two excitation frequencies are suppressed.

The origin of these two signals is unknown at this time. The possibility that they are the result of some hybrid resonance is doubtful at the pressures these

experiments were performed (≤ 1 Torr). Further studies seem to indicate that they are atomic in nature. First of all, they "grow in" as the pressure in the heat pipe is decreased, similar to the known atomic resonances (figure IV-17). Second, when the dye laser is tuned to the ? signal, weak conical emission is observed suggesting that it is part of an atomic wave-mixing process. Another piece of puzzling evidence is the fact that they are also observed in the ionization spectrum at low pressures (figure IV-17).

Chapter V

Summary

This thesis has demonstrated the use of multiphoton spectroscopy to investigate a number of different processes in rare gases and alkalies. In chapter II, a novel method to investigate collision processes was introduced. This method took advantage of multiphoton selection rules to populate select levels in xenon and investigate disalignment and dephasing of these levels as a result of collisions with ground state xenon atoms. As stated earlier, this method can be extended in other directions to investigate collisional interactions between similar and dissimilar gases. Another possible extension could involve examining how collisional dephasing affects ionization yield of an alkali in a heat pipe environment.

Chapter III dealt with investigating excited states of rare gases and some molecules by employing multiphoton ionization photoelectron spectroscopy. Energy analysis and angular distribution measurements of the outgoing electron has proven to be a sensitive method of examining the nature of the intermediate level as well as the resulting ion in a resonantly enhanced multiphoton ionization process.

Comparison of experimental results with theory is needed to understand the exact nature of intermediate levels

and the dynamics of the multiphoton ionization process. In this work, it was shown that, although theory was able to predict certain aspects it still needs to be refined, in order to better understand the multiphoton process.

Chapter IV looked at a number of different optical processes in dense alkali vapors. The underlying theme in all of the processes observed was the conversion of the incident laser light to other frequencies. Understanding of the various processes can lead to generation of new and intense light sources at frequencies that are not currently available commercially.

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