

ONE- AND TWO-COLOR LASER SPECTROSCOPY WITH  
PHOTOACOUSTIC AND MULTIPHOTON IONIZATION DETECTION

Thesis by

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Abstract

The techniques of pulsed photoacoustic spectroscopy and multiphoton ionization spectroscopy have been used to study several types of weak optical transitions in the ultraviolet or visible spectral regions for gas phase molecules. Both one- and two-color experiments have been performed. The one-color experiments involved the study of high vibrational overtones and spin-forbidden transitions. The two-color experiments demonstrated the application of photoacoustic detection of stimulated emission pumping for populating high vibration levels of the ground electronic state. Two-color experiments were also used to study excited state absorption processes in aniline.

Pulsed laser photoacoustic spectra of  $\text{CD}_3\text{H}$  in the region of the  $\Delta\nu_{\text{CH}} = 5, 6, \text{ and } 7$  CH stretch overtones were obtained. These overtones and nearby combination bands displayed sharp rotational structure, indicating a minimum excited state population relaxation time of  $5 \times 10^{-12}$  sec. A combination sum analysis was used to generate excited state rotational constants  $B'$ . These constants reflect the geometries of the excited states, and therefore provide a sensitive probe of the mixing between various zero order excited states.

Photoacoustic detection was used to monitor a stimulated emission pumping process in p-difluorobenzene. Using the

$\tilde{A}^1B_{2u}$  5' state as an intermediate state, several vibrational levels of the ground electronic state were populated. The photoacoustic technique is an attractive alternative to other techniques because of its sensitivity, simplicity, and its ability to differentiate between stimulated emission pumping and excited state absorption.

Time-resolved excited state absorption studies were performed on aniline using the multiphoton ionization and photoacoustic detection techniques. Signals from both of these techniques were measured as a function of the time delay between two laser pulses of different wavelength. The first pulse excited the  $S_1$  0-0 transition. The second pulse excited either  $S_1$  or a triplet state produced by intersystem crossing, depending on the time delay between pulses. Both ionization and dissociation processes were observed. By varying the conditions of excitation, it appears that a given amount of energy can be selectively channeled into either ionization or dissociation pathways. These results were explained using a simple Franck Condon factor model.

The application of pulsed laser photoacoustic spectroscopy to the study of weak absorptions in the visible and ultraviolet spectral regions was investigated. Photoacoustic spectra of triplet states in  $CS_2$ ,  $SO_2$ , biacetyl, and thiophosgene were obtained. An attempt to detect the  $\tilde{a}^3B_{1u}$  state in benzene, produced instead a two-photon spectrum of several Rydberg states. It was discovered that the sensitivity of

the pulsed photoacoustic technique for extremely weak absorptions is limited by the increased probability of multiphoton absorption when high intensities are used.

Finally, in two appendices, the detection of the  $\bar{a}^3A_2$  state in  $CS_2$  by the multiphoton ionization technique is presented. The  $CS_2$  study demonstrates the utility of the multiphoton ionization technique for detecting spin-forbidden transitions at high resolution and with great sensitivity.

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## Introduction

The experimental work described in this thesis is concerned primarily with the detection of weak optical absorptions in the gas phase. The optical transitions studied in the course of this research were weak for one of the following reasons. (1) The absorption involved a multi-quantum vibrational transition in the ground electronic state. (2) The transition resulted from stimulating emission out of a sparsely populated electronic state back to the ground electronic state. (3) The transition involved an excited state absorption process from an electronic state with a small population. (4) The absorption resulted from a spin-forbidden transition between states of different spin multiplicities.

The results presented in papers I-IV are spectroscopic studies of transitions from each of the above four categories, respectively. They were obtained using the photoacoustic spectroscopy (PAS) or multiphoton ionization (MPI) detection techniques. These techniques will be described briefly in the next two sections.

### Photoacoustic Spectroscopy

The photoacoustic effect was first described in detail by Alexander Graham Bell in 1881.<sup>1</sup> Recently, due to the widespread availability of lasers, it has been used extensively in studies of gases, as well as liquids and solids. Excellent reviews of this technique can be found in books

published by Pao<sup>2</sup> and Rosencwaig.<sup>3</sup>

In a typical gas phase photoacoustic experiment, an intensity-modulated light beam is directed into a chamber containing the gas sample to be studied. If the sample absorbs some of the incident light, the molecules excited by the absorption process may undergo collisional deactivation. Eventually, some of the initially absorbed energy appears as translational energy of the molecules and is detected by a microphone as a periodic pressure increase. Recording the microphone signal as the wavelength of the incident light is scanned produces a photoacoustic spectrum.

In the PAS experiments described in this thesis, a tunable pulsed dye laser was used as the excitation source. Molecules excited by a <10 nsec pulse from this laser typically undergo collisional relaxation in a few  $\mu$ sec. A local pressure increase appears in the region of the laser beam. This pressure increase propagates radially outward as a cylindrical pressure wave. It is detected when it strikes a microphone mounted in the wall of the photoacoustic cell. A pulsed laser photoacoustic spectrum is generated by monitoring the amplitude of this pressure wave as a function of excitation wavelength.

The PAS technique has been used widely in the study of weak absorptions arising from high vibrational overtone transitions,<sup>4,5</sup> detection of atmospheric pollutants,<sup>6,7</sup> and

and excited state absorption.<sup>8,9</sup> We have used the pulsed PAS technique to investigate both high vibrational overtones and spin-forbidden transitions. Paper I presents the results of a pulsed PAS study of high vibrational overtones of CD<sub>3</sub>H. The resolved rotational structure in these spectra permitted rotational analysis which generated the excited state rotational constants B'. Since these constants reflect the geometry of the excited state, they provide a sensitive probe of the mixing between various zero order vibrational states. Paper IV presents a discussion of the applicability of the pulsed PAS technique for studying extremely weak spin-forbidden transitions to triplet states. Several examples of triplet state spectra obtained using the pulsed PAS technique are given to illustrate the advantages and disadvantages of that technique.

A second, completely different class of PAS experiments focuses on the dynamics of excited states in molecules. Since the PAS technique is sensitive to the nonradiative decay of excited molecules, it provides a unique tool for studying excited state dynamics. The wide variety of problems studied in the past includes investigation of vibrational relaxation rates,<sup>10</sup> thermochemical effects following dissociation,<sup>11</sup> electronic relaxation kinetic effects,<sup>12</sup> and radiationless transitions.<sup>11,13</sup> All of these studies used a CW laser PAS technique in which the change of phase angle of

the PAS signal with respect to the intensity modulation was monitored. This method permits time-resolution studies in the 100  $\mu$ sec timescale or slower. We have developed a new gas phase two-color time-resolved pulsed PAS technique which permits a new class of dynamics experiments to be performed with nanosecond or faster time resolution. Briefly, the output beams of two pulsed dye lasers are overlapped inside a photoacoustic cell in a collinear counterpropagating configuration. The time delay  $\Delta t$  between the output pulses of the two lasers can be adjusted with nanosecond precision. The first pulse can excite an electronic state of the sample molecules, which can fluoresce or nonradiatively transfer to another state through internal conversion or intersystem crossing. Depending on the value of  $\Delta t$  chosen, the second pulse will find molecules in the ground state, the state initially excited by the first pulse, or some other state populated by a radiationless process. If the molecules are in an excited state, the second pulse may be absorbed in an excited state absorption process, or stimulate emission out of the excited state down to a lower state in the molecule. Since the PAS technique responds to the total amount of energy deposited in the sample, the excited state absorption or stimulated emission processes produce larger or smaller PAS signals, respectively. Varying the wavelengths of the laser pulses, or changing  $\Delta t$ , while monitoring the PAS signal allows

a new and versatile technique for studying excited state dynamics.

Paper II describes the use of the two-color time-resolved PAS technique to populate high vibration levels of the ground electronic state of p-difluorobenzene using stimulated emission pumping. The increase or decrease in the photoacoustic signal provides a simple method for determining whether stimulated emission or excited state absorption has occurred.

Paper III presents a study of excited state absorption in aniline performed using the two-color time-resolved PAS technique and a MPI technique. Absorption from both  $S_1$  and a vibrationally excited triplet state produced by intersystem crossing to states lying above the adiabatic ionization potential was studied. It was discovered that a given amount of excitation energy can be selectively channeled into either ionization or dissociation, depending on the way in which the energy is deposited in aniline.

### Multiphoton Ionization Spectroscopy

When very intense photon fields interact with a molecule multiphoton absorption processes become highly probably. Under these conditions, the molecule may be excited above the ionization potential and subsequently ionize. In typical MPI experiments, an intense UV or visible laser pulse is

focused into a gaseous sample, producing an ionization current which is measured as a function of wavelength. When integral multiples of the photon energy are resonant with states in the sample, an increase in ionization current occurs.

MPI spectroscopy has primarily been applied to the study of two-photon excited states in molecules such as benzene,<sup>14,15</sup> 1,3-butadiene,<sup>16</sup> hexatriene,<sup>17</sup> etc. Recent MPI experiments have detected the masses of fragments produced and/or the kinetic energy of released electrons in molecules such as NO,<sup>18,19</sup> I<sub>2</sub>,<sup>18,20</sup> H<sub>2</sub>S,<sup>21</sup> NH<sub>3</sub>,<sup>22</sup> benzene,<sup>18,20,23,24</sup> acetaldehyde,<sup>25</sup> aniline,<sup>26</sup> azulene,<sup>27</sup> naphthalene<sup>27</sup> and organometallics.<sup>28</sup>

Paper III presents a study of aniline which used the MPI technique to complement the results obtained with the two-color time-resolved photoacoustic technique. In the MPI experiments, the wavelengths of the two-laser pulses and  $\Delta t$  were also varied, but an ion current was detected instead of a photoacoustic signal. The combination of both MPI and PAS detection in these experiments provided a powerful method for probing excited state dynamics above the ionization potential.

Appendix D contains a paper which describes the use of a MPI technique to detect spin-forbidden transitions in CS<sub>2</sub>.<sup>29</sup> The  $\tilde{a}^3A_2$  state of CS<sub>2</sub> was detected using a one-photon spin-forbidden transition as a rate limiting initial step. Subsequent absorption of additional photons through the triplet

manifold ionized the molecule. Therefore, by measuring the ionization current as a function of laser wavelength, the spectrum of the  $^3A_2$  state was generated. This technique promises to allow measurement of spin-forbidden transitions with great sensitivity and high resolution.

A description of the laser systems and related electronics used in the PAS and MPI experiments is contained in Appendix A. Appendix B contains a description of the photoacoustic cells used in these experiments and summarizes the important criteria for optimizing cells for pulsed laser excitation. Appendix C contains a discussion of wavelength conversion by stimulated Raman scattering (SRS), and a description of a high pressure cell for SRS in  $H_2$ .



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