Infrared and Visible Laser Double Resonance Studies of Vibrational Energy
Transfer Processes in Polyatomic Molecules

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FINAL REPORT

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Jackson, MS 39217.

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by

Dr. Ravi Bhatnagar
Department of Chemistry,
Texas Southern University,
3100 Cleburn Avenue,
Houston, TX 77004.

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Progress Report (June 15, 1988 - June 14, 1991)

The original award was to Jackson State University and covered the period of June 15, 1988 through June 14, 1991. The principle investigator's laboratory was equipped with a pulsed CO₂ laser (Gen-Tec model DD250) and a nitrogen pumped dye laser (Laser Photonics model UV24-DI16) which formed the core of the equipment required to conduct the research work proposed in the original proposal. The reaction chamber along with the vacuum pumps, photomultiplier - spectrometer and data collection electronics were also available at Jackson State University. During the first year of the project, the CO₂ laser was refurbished by polishing the electrodes, removing corrosion from the cooling tubes and replacing old optics. The inside of the laser chamber was cleaned and the chamber resealed. The laser was realigned and the output pulse energy close to the original specification obtained.

The probe laser was a newly acquired nitrogen laser pumped dye laser which was installed during the early part of this project. The dye laser was capable of producing 1.8 mJ/pulse and frequency doubling of this output energy was attempted using Beta-Barium Borate (BBO) crystal in order to generate laser energy in the ultraviolet region. The frequency doubling efforts were successful and produced ~ 28 μ J/pulse at 250 nm. Output energy as high as 75 μ J/pulse were observed but the crystal was damaged due to high laser intensity in the focal region. The crystal housing window was also damaged and had to be replaced. Further details on this work are included in a dissertation submitted as a part of the M.S. (Chemistry) degree by Mr. Mehrdad Mehdood. An abstract of this thesis is enclosed in the appendix 1. During this period s-tetrazine was synthesized which was one of the molecules chosen for the vibrational energy transfer studies. The second annual report, appendix 2, contains additional information on this aspect of the work.

In August 1990, the principle investigator accepted a faculty appointment in the chemistry department at Texas Southern University in Houston, Texas. It was necessary to move both lasers and some of the equipment from Jackson State University to Texas Southern and install them again. However, the vacuum system and data collection electronics belonged to Jackson State University and hence

the gas phase work could not continue at Texas Southern University. Due to this unforeseen problem, principle investigator decided to study the spectroscopy of chromylchloride in dilute solutions in collaboration with the Center for Fast Kinetics (CFKR) at the University of Texas at Austin. The department of energy was informed of this change in the direction of the original proposal via a letter to the technical monitor, Dr. William H. Kirchhoff (copy of letter enclosed).

Spectroscopy of Chromylchloride

Preliminary emission and excitation spectra have been recorded by the P.I. using a Perkin-Elmer Model LS-5 fluorescence spectrometer. These results show unusually well resolved vibronic structure in the emission spectrum as shown in Figure 1. The most significant finding of this preliminary research is apparently simultaneous luminescence emission involving transitions from a series of excited electronic states directly to various vibrational levels in the ground electronic state as shown in Figure 2. If confirmed, such simultaneous emissions from higher electronic states directly to the ground electronic state will constitute a violation of Kasha's rule [1]. The electronic spectrum and structure of chromylchloride has been of interest to spectroscopists for many years [2-7], and more recently the multiple photon excitation of this molecule by a pulsed CO_2 laser and the analysis of the resulting fluorescence has been the subject of interest for several research groups [8-14]. Karny et. al. [10] first reported evidence that collisionless infrared multiple photon pumping of chromylchloride by a focused CO_2 laser produced a bound electronic state lying below the ground state dissociation limit. The resulting visible fluorescence with peak intensity at 630 nm, was assigned primarily to the electronically excited parent molecule. Nieman and Ronn [11] attributed this phenomenon to inverse electronic relaxation which was theoretically suggested by Nitzan and Jortner [12]. The origin of the fluorescence emitted by vibrationally excited CrO_2Cl_2 has also been examined and discussed by Burak and Tsao [13] and Tsao et al. [14] and it is believed that both the parent molecule and a dissociation product, CrO_2Cl , may significantly contribute to the fluorescence under certain conditions. Heller and West [15] have studied the vibrational quasi-continuum in CrO_2Cl_2 using a frequency

doubled Nd^{+3} : YAG laser (532 nm) in conjunction with a pulsed CO_2 laser. Bhatnagar et. al. [16] carried out a series of experiments, including some infrared-visible laser double resonance measurement on CrO_2Cl_2 in order to probe the time behavior of the vibrationless ground state and the flow of excess energy within various vibrational manifolds of the molecule. Bhatnagar et. al. [16] also established the dissociation energy threshold for CrO_2Cl_2 at 0.45 J/cm^2 using a mass spectrometer to monitor the appearance of the dissociation products as a result of the CO_2 laser irradiation. Recently, Sowinska et. al. [17] have studied the electronic absorption spectrum of chromylchloride dissolved in CCl_4 and acetone. The spectral contours were analyzed using digital filtering, curve fitting techniques and Frank-Condon factors. Their studies revealed that the vibronic structure corresponded with the O-Cr-O chromophore and that the vibrational frequencies and anharmonicity of the progressions in chromylchloride solutions are very close to those in the vapor phase.

Electronic absorption spectra reported by Sowinska et.al. (17) were reproduced, figure 3, to confirm the reproducibility of the observed peaks. Further investigations of the luminescence emission and excitation spectra were carried out over a range of wavelengths between 350 nm and 700 nm. Two such emission spectra are included here. Figure 4 is the emission spectra observed following excitation at 476 nm and figure 5 is the emission spectra corresponding to excitation at 350 nm. Systematic variation in the excitation wavelength has been carried out between 350 nm and 550 nm and several of these spectra are included in the dissertation submitted to Jackson State University by Mr. Sanjay Kamtekar. A summary of all observed features in the emission bands is presented in Table 1. However, there are no spectroscopic studies of chromylchloride solutions reported prior to this study and there exists a strong need to conduct more thorough investigations of fluorescence and phosphorescence emission in chromylchloride solutions.

We have not recorded electronic state life times at the present time to distinguish phosphorescence emission from the fluorescence emission but such investigations should be carried out in the future. We also suggest further studies using a higher resolution spectrometer and at low sample temperatures (77^0 K) to remove "hot band"

transitions. Finally, Laser induced fluorescence measurements at low temperatures will be required to precisely locate various electronic band origins and understand all the photophysical processes taking place in this molecule.

Figure 1: Fluorescence excitation spectrum of chromylchloride in CCl_4 .

DATE: 03/15/91
 TIME: 20:14:36.62
 FILENAME: RAVI69
 EXCIT. WAVELENGTH: 444
 INTEGRAL:
 160573.1563

Figure 2: Fluorescence emission spectrum from chromylchloride in CCl_4 following excitation at 444nm.

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4: 6 PM 6/ 7/91

TITLE: P0013-5

700.0 nm

0.0575 Abs

CURSOR DATA :

◀◀	◀	▶	▶▶	EXPAND	SET
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Figure 3: Absorption spectrum of chromylchloride in CCl_4 .

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Figure 4: Fluorescence emission spectrum from chromylchloride in CCl_4 following excitation at 476nm .

Figure 5: Fluorescence emission spectrum of chromylchloride in CCl_4 following excitation at 350nm.

Table 1
Summary of Observed Emission Bands

Excitation Wavelength nm	cm ⁻¹	Observed Emission Peaks nm
560	17857.00	Probable peaks at 590 and 670 nm.
557	17953.3	610nm, 665 nm, 675 nm.
550	18181.8	654 nm.
530	18868.0	No significant emission.
515	19417.5	565 nm and 610 nm.
504	19841.3	565 nm and 610 nm.
496	20161.3	568 nm.
490	20408.0	528 nm and 565 nm.
476	21008.4	527 nm, 567 nm and 610 nm.
470	21276.5	530 nm (shoulder at 540), 568 nm and weak band at 625 nm.
464	21552.0	534 nm, weak bands at 568 nm and 620 nm.
460	21739.0	530 nm + weak bands at 568 nm and 620 nm.
455	21978.0	527 nm + weak band at 565 nm.
452	22123.8	525 nm + 568.5 nm and weak band at 608 nm.
444	22522.5	527 nm + 565 nm and weak activity at 610 nm.
435	23256.0	529 nm, 532 nm, 544 nm and weak bands at 610 nm.
430	23256.0	497 nm, 532 nm, 544 nm and several bands around 600 nm.

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FREQUENCY DOUBLING OF NITROGEN LASER PUMPED DYE
LASER USING BBO CRYSTAL

BY
MEHRDAD MAHDOOD

Approved by :

R. Bhatnagar

Major Advisor & Chair
of Thesis Committee

S. Samani

Member

Eric A. Moe

Member

Odyssey Touloukian

Member

R. Venkatesan

Member

L. H. Sullivan / Cass D. Ocker

Department Chair

Leslie Paul McLeone / ECF

Dean of Graduate School

ABSTRACT

FREQUENCY DOUBLING OF NITROGEN LASER PUMPED DYE LASER USING BBO CRYSTAL

(August, 1990)

By

MEHRDAD MAHDOOD

Department of Chemistry

Chemical Physics Program

Jackson State University

Jackson, MS 39217

ADVISOR: DR. RAVI BHATNAGAR

Second harmonic generation (frequency doubling) of a nitrogen laser pumped dye laser has been successfully achieved in a negative uniaxial crystal, Beta Barium Borate. The laser system has produced sufficient energy in the ultraviolet region that can be used either to treat eye disorders or to perform time resolved kinetics experiments.

The maximum output energy of 57 μ J has been obtained at 250nm wavelength using Coumarin 500 dye. The ultraviolet output energy is significantly greater than that obtained with other crystals such as KD*P and ADP. The ultraviolet output has also been obtained at several different wavelengths. Overall performance of second harmonic generation conversion efficiency of Beta Barium Borate including all affecting factors is evaluated to maximize the pulse output. The second harmonic generation efficiencies in this study are compared with other nonlinear materials performances available in literature.

**INFRARED AND VISIBLE LASER DOUBLE RESONANCE STUDIES OF
VIBRATIONAL ENERGY TRANSFER PROCESSES IN POLYATOMIC MOLECULES**

PROGRESS REPORT

(JUNE 15, 1989 - PRESENT)

Dr. Ravi Bhatnagar

Chemistry Department

Jackson State University

Jackson, MS 39217

This progress report covers the second year (June 15, 1989 - June 14, 1990) of a three year project awarded to Jackson State University. The project has progressed satisfactorily during this period and we have been able to achieve some of the goals outlined in the last years progress report.

We have completed the repairs on the CO₂ laser, installed new output mirror and tested the vacuum chamber. We have replaced the diffusion pump connected to the vacuum chamber and it is now possible to evacuate it to better than 10^{-6} torr. We have also purchased a new probe laser (Nitrogen laser pumped dye laser) from Laser Photonics for use in this project. The new laser is already installed and tested with several dyes. We have acquired two frequency doubling crystals, KDP and BBO and at this time we are conducting experiments to optimize their performance. The frequency doubling capability will extend the useful range of our dye laser in the ultra-violet region. We intend to use this

capability at a later stage to study the reaction dynamics of free radicals generated by the CO₂ laser pulse.

We have synthesized s-tetrazine (1) in our laboratory and although the yield was poor, we were successful in our attempt. The compound is unstable over a long period of time and due to the cost of chemicals involved, we have postponed further synthesis until all our equipment is ready for an experiment. The data processing software (ASYST 2.0) has been upgraded to ASYST 3.1 and we are in the process of interfacing the computer system to the signal averager. In addition, we are also developing a scan-drive to control the dye laser wavelength and automate the operation of the dye laser. This will enable us to synchronize the pump and the probe laser and generate the excitation spectrum in a reproducible manner. The computer will also control other aspects of our experiment. We are also conducting computer-assisted literature searches on a regular basis and utilizing inter-library loan facility to keep up with the current developments in this area. I have attended the conference organized by the Optical Society of America and held in Los Angeles in January 1990. The conference was very useful and allowed me to attend many sessions on new laser systems and interact with several scientists involved in a broad variety of research projects. I was also able to look at new products in the market.

The project has supported two graduate students during this year and I expect one of them to complete his dissertation for the M.S. degree by the end of summer 1990. The second student will be able to complete his work by the end of 1990. The stu-

dents have been trained in the proper use of lasers and other laboratory techniques. They are also using the computer system for word-processing in addition to learning the ASYST software.

During the next budget year (June 15, 1990 to June 14, 1991) we intend to make the following progress :

- Complete the frequency doubling of the dye laser using BBO crystal.
- Complete the computer interfacing of the data collection electronics.
- Align the reaction chamber with the pump and probe lasers and the spectrometer.
- Conduct preliminary experiments with chromylchloride.
- Synthesize s - tetrazine again and investigate the energy transfer processes as outlined in the original proposal.
- Continue literature search for new molecules which could be studied with this technique.

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TEXAS SOUTHERN UNIVERSITY
3100 CLEVELAND AVENUE HOUSTON, TEXAS 77004

(713) 527-7004/639-1914

Department of Chemistry

March 11, 1991

Dr. William H. Kirchhoff
Fundamental Interaction Branch
Division of Chemical Sciences
Office of Basic Energy Science
Department of Energy
Washington, D.C. 20545

Dear Dr. Kirchhoff,

As you are aware, I am now with the Chemistry Department of Texas Southern University in Houston, Texas. I came here in August 1990 but I could transfer my equipment only at the end of November due to clearance formalities at Jackson State University.

I have since been exploring various options available to me in terms of conducting research within the outline set forth in the original proposal. I could not carry on the gas phase work because the vacuum pumps available to me at Jackson belonged to the department. In fact, most of the electronics and data processing system including the photomultiplier tube also belonged to Jackson State and it made it impossible to carry out the project further. However, I learned about the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin which is a NIH supported facility designed for external use. I visited CFKR in September to see their facilities. It has several laser systems and all the necessary technical support but they work primarily in the liquid phase. With that in mind, I decided to look at the spectroscopy of chromylchloride in various solvents. There has been quite a lot of work on the spectroscopy of chromylchloride in the gas phase including a proposed inverse electronic relaxation mechanism to account for the visible fluorescence as a result of the CO₂ laser induced multiple photon absorption. Recently, there was a report on the vibronic structure observed in dilute solutions of chromylchloride in Acetone and we have been able to reproduce that here. In the mean time, I have also designed a photoacoustic cell to measure the absorbed energy and perhaps obtain fluorescence quantum yield data later. I am going to conduct fluorescence emission and excitation measurements at Austin during my springbreak. I hope to collect sufficient data to clarify the effect of solvents on the electronic energy levels in chromylchloride.

I would like to thank you again for your support of this project. The situation at Texas Southern is totally different as compared to Jackson State. The university is located within a mile of the University of Houston with its excellent library and technical support facilities. I hope to develop collaborative arrangement with some chemistry faculty at the University of Houston for future projects. I will send you final report as it becomes due but if you need further information, please do let me know.

Yours Sincerely,

R. Bhatnagar

FLUORESCENCE SPECTROSCOPY OF CHROMYL CHLORIDE
IN DILUTE SOLUTIONS

A THESIS

By

SANJAY D. KAMTEKAR

Approved by:

K. P. Bhargava / 1003

Major Advisor & Chair
of Thesis Committee

B. Chak

Member

E. M. C.

Member

R. Venkatesan

Member

Henry Lewis / 1003

Member

Carol D. Fair

Dept. Chair

Betha Fletcher / 1003

Dean of Graduate School

July 1991

ABSTRACT

FLUORESCENCE SPECTROSCOPY OF CHROMYL CHLORIDE IN DILUTE SOLUTIONS

The spectroscopy and molecular structure of chromyl chloride has been of interest to scientists for a long time. Conventional spectroscopic studies have been carried out in the vapor, pure liquid and solid phases and also in low temperature matrices. However there is only one published study of visible absorption spectrum of dilute solutions of chromyl chloride in acetone and CCl_4 . Interest in the behavior of chromyl chloride molecule renewed during the last decade when the possibility of inverse electronic relaxation following the CO_2 laser induced multiple photon absorption was reported. In spite of considerable work on this molecule, there are many unanswered questions about the nature of various electronic states and photophysical processing occurring in chromyl chloride.

We report here visible luminescence emission and luminescence excitation spectra of dilute solutions of chromyl chloride in carbon tetrachloride, acetone and phosphorous oxychloride. Well resolved vibronic structure in the excitation spectrum is observed and we have recorded emission spectra following excitation of selected electronic transitions. Although, hot bands transitions complicate the observed spectra an attempt has been made to assign various transitions and identify band origins. Suggestions for future work are also included.

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Name of Presenter: Dr. Ravi Bhatnagar
Institution: Texas Southern University, Chemistry Department
Address: 3100 Cleburne Ave.
Houston, Texas 77004

Telephone Number: (713) 639-1914

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☐ Environmental Science	☐ Evolutionary Biology
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☐ Geology	☐ Management

FREQUENCY DOUBLING OF N₂-LASER PUMPED DYE LASER USING

B.B.O. CRYSTAL. R. Bhatnagar*, Chemistry Department, Texas Southern University, Houston, Texas 77004.

Recently Beta-Barium-Borate (B.B.O.) crystal has been used for second harmonic generation from a YAG laser. It is shown that the crystal has high conversion efficiency and high damage threshold. The B.B.O. crystal has been used in this study to generate tunable ultraviolet radiation from a low power N₂-laser pumped dye laser system.

Output energies in excess of 50 μ J/pulse have been obtained at 250nm. Complete results will be presented over the tunable range of the system, from 220nm to 300nm.

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☐ Environmental Science	☐ Evolutionary Biology
☐ Freshwater and Marine Science	☐ Terrestrial Ecology and
☐ Geology	☐ Management

VIBRATIONAL ENERGY TRANSFER PROCESSES IN SF_6 + METHYLGLYOXAL. R. Bhatnager*, Chemistry Department, Texas Southern University, Houston, Texas 77004.

Vibrational energy transfer processes in gas mixtures of SF_6 and methylglyoxal have been studied using an infrared-visible double resonance technique. The CO_2 laser pumping of SF_6 is used to create vibrationally excited methylglyoxal molecules in a collisional energy transfer from SF_6 . The fluorescence emission from methylglyoxal has been used to monitor population changes in various ground vibrational levels. Computer analysis of the data is used to obtain various rate constants.

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