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NONLINEAR OPTICAL SPECTROSCOPY OF MOLECULAR COMPLEXES'
(U) OREGON STATE UNIV CORVALLIS DEPT OF CHEMISTRY
J M NIBLER DEC 86 AFOSR-TR-87-0047 AFOSR-85-0059

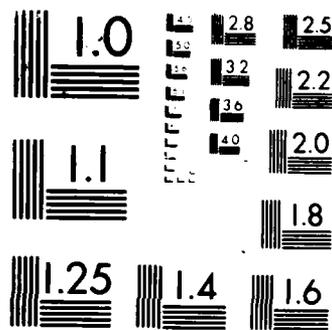
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MICROCOPY RESOLUTION TEST CHART

PORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE						
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR-87-0047			
6a. NAME OF PERFORMING ORGANIZATION Oregon State University		6b. OFFICE SYMBOL <i>(If applicable)</i>	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC			
6c. ADDRESS (City, State and ZIP Code) Dept of Chemistry Corvallis, OR 97339			7b. ADDRESS (City, State and ZIP Code) Bldg 410 Bolling AFB DC 20332-6448			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL <i>(If applicable)</i> NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-85-0059			
8c. ADDRESS (City, State and ZIP Code) Bldg 410 Bolling AFB DC 20332-6448			10. SOURCE OF FUNDING NOS.			
			PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2917	TASK NO. A2	WORK UNIT NO.
11. TITLE (Include Security Classification) Nonlinear Optical Spectroscopy of Molecular Complexes (U)						
12. PERSONAL AUTHOR(S) Joseph W. Nibler						
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Yr., Mo., Day) 86 12		15. PAGE COUNT 6
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Raman Spectroscopy Clusters <i>water hydrogen clusters</i>			
FIELD	GROUP	SUB GR				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A Coherent Raman Loss Spectrometer was set up and used to obtain spectra of static and jet samples of CO ₂ at 0.003 wavenumber resolution. Coherent Raman methods were used to examine small hydrogen bonded clusters of HCN in static samples and in jet expansions. The first Raman data for a hydrogen bonded complex formed in jets was obtained, and preliminary studies of H ₂ O and HCL jet expansions have been done. CARS spectra of van der Waals complexes were taken. In the CO ₂ dimer case the most stable conformation was found to be an offset parallel shape rather than the polar T form suggested by others previously. The first CARS detection of a low frequency intramolecular librational mode was made of the CO ₂ dimer. The energy distributions of NO and CF ₃ photofragments of CF ₃ NO were studied using CARS as a probe technique. This was the first detection of CF ₃ radical by Raman methods. The photodissociation of this molecule in low temperature argon matrices was also studied. <i>OTIC FILE COPY</i>						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input checked="" type="checkbox"/> OTIC USERS <input type="checkbox"/>				21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr Francis J. Wodarczyk			22b. TELEPHONE NUMBER (Include Area Code) (202) 767-4963		22c. OFFICE SYMBOL NC	

AFOSR-TR- 87 - 0047

NONLINEAR OPTICAL SPECTROSCOPY OF MOLECULAR COMPLEXES

FINAL REPORT

AFOSR-85-0059

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DEPARTMENT OF CHEMISTRY
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FINAL REPORT - AFOSR/DoD University Instrumentation Program

Grant No. AFOSR-85-0059

Title: Nonlinear Optical Spectroscopy of Molecular Complexes

Submitted by: Joseph W. Nibler
Chemistry Department
Oregon State University

I. Equipment Purchased

A. Coherent Radiation Ring Dye Laser and Argon Ion Pump Laser

1.	Innova 90-5 Argon Ion Laser (Demo Unit with 15% disc.)	\$20,800
2.	CR-699-21 Actively Stabilized Scanning Single Frequency Ring Dye Laser	48,000
	Shipping	300
	System Discount	(4,800)
	Total, item A	\$64,300

B. Cooper LaserSonics (Molelectron) Nd-YAG Single Mode Laser

1.	MY34 (10 Hz) Oscillator/Amplifier	\$48,000
2.	MY-SAM Single Axial Mode Accessory	7,500
3.	MY-SHG Second Harmonic Generator	5,000
4.	MY-THG Third Harmonic Generator	3,000
	Shipping	320
	System Discount	(7,620)
	Total item B	\$56,200

AFOSR Contribution (This Grant)	Item A	\$64,300
	Item B	\$15,700

Total AFOSR expenditure \$80,000

II. RESEARCH APPLICATIONS OF THIS EQUIPMENT

This report summarizes briefly some of our research activities since the award of this equipment grant on 15 Dec. 1984. The work on molecular clusters (B, C, D) was supported by AFOSR contract F49620-83-C-0007 and by NSF grants CHE-8209968 and CHE-8511793. The latter provided all of the operational funds for projects D, E, F.

A. High Resolution Stimulated Raman Loss Studies

George Pubanz, Rainer Beck and Dr. Jeng Yang have set up the Coherent Raman Loss Spectrometer funded by this grant. The system is based on a ring dye laser, pulse amplified with a Nd-YAG pumped amplifier, and combined with a single mode argon ion laser which serves as the probe laser. Most of the initial work involved construction of the pulse amplifier network and the integration of this with all of the commercial components. With this system, for example, George Pubanz has obtained excellent spectra of static and jet samples of CO_2 at 0.003 cm^{-1} resolution, and part of this developmental work is documented in his Ph.D. thesis (1986). The lasers have also been used at various times to provide a high resolution capability for some of the projects in B to E below.

The Spectrometer is still evolving. Chris Walker, an unusual undergraduate (triple BS degree in EE, Physics and Computer Science - now on a Navy Graduate Fellowship at Cornell in Physics), joined us on this project last year and was very helpful in improving the electronic detection system and in modifying the ring dye laser computer control software for more efficient data processing. Currently work is underway to reduce residual RFI and acoustic noise and to increase the cluster concentrations in jets by nozzle changes for operation with a slit orifice at higher driving pressures. We also plan to modify the system for easy conversion between CARS and stimulated Raman measurements and to provide an injection locking capability to improve the longterm frequency stability of the Nd-YAG laser for the CARS experiments

B. CARS Spectra of Hydrogen-Bonded Complexes in Free Jets.

This project was a collaboration with Prof. Tom Dyke of the University of Oregon, whose work concentrated on the microwave spectra of hydrogen bonded species. At Oregon State University, Glen Hopkins and Dr. Mark Maroncelli have used Coherent Raman methods (CARS and PARS) to examine small hydrogen bonded clusters of HCN in static samples and in jet expansions. We were successful in obtaining the first Raman data for a hydrogen bonded complex formed in jets and were able to determine several vibrational frequencies for the dimer and trimer species. FTIR data indicate that the trimer is linear rather than cyclic as had been proposed by some workers. More details are included in Ref. 2,3. Some preliminary studies of H_2O and of HCl jet expansions have been done by Nancy Triggs and Glen Hopkins and we hope to continue with this effort pending approval of an AFOSR renewal proposal.

C. CARS Spectra of Van Der Waals Complexes in Free Jets.

This is an effort to develop CARS for the study of van der Waals complexes and we are encouraged with the progress on this project so far. Dr. Mark Maroncelli and George Pubanz were able to obtain Raman data for the CO₂ dimer, formed in expansions as dilute as 1% in Helium. Dilution and jet temperature variations allowed us to distinguish dimer bands from those of higher aggregates and comparisons with IR data of Kopec and Ewing led to the conclusion that the most stable conformation is a C_{2h} offset parallel shape, rather than a polar T form suggested by some workers. This work is described in Ref. 4, 7, 9. Similar studies of other dimeric species and Ar--X complexes is being pursued by Nancy Triggs and Dr. Jeng Yang, a UCLA student of Prof. El-Sayed who joined us last year.

C. Low Frequency CARS Spectroscopy.

Nancy Triggs, Brian Bozlee, and Dr. Jeng Yang have set up a folded BOXCARS phase matching arrangement to permit us to do low frequency spectroscopy over the range from 0 to 700 cm⁻¹. Excellent spectra are obtained at high resolution even down to 0 cm⁻¹ shift and the sensitivity is such that jet spectra are easily obtained for monomeric species (ref.8). Most exciting to us is our recent observation of a weak cluster band in CO₂ expansions which we believe may be the Raman active librational mode of the dimer. Work to confirm this first CARS detection of a low frequency "intramolecular" mode is continuing and is being supplemented by Kyung Lee in Raman matrix isolation studies of similar motions of the dimer formed in inert gas hosts. We also intend to use the low frequency CARS apparatus to study high temperature species such as inorganic salts, vaporized in static and free jet expansions.

D. Photochemistry

Brian Bozlee completed a study of the energy distributions of the NO and CF₃ photofragments of CF₃NO using CARS as a probing technique. The NO fragment was found to be very hot rotationally in accord with laser excited fluorescence results of others. The corresponding distribution in the symmetric stretch of the CF₃ was measured in this first detection of this pyramidal radical by Raman methods. The energy distributions were found to be in good agreement with those calculated on a statistical basis and these results are reported in reference 6. Further work on such systems is continuing and Marty Robbins, a chemistry undergraduate, has spent the summer preparing CF₃N=NCF₃, an azo compound which we expect to undergo sequential fragmentation on UV excitation to produce N₂ + 2 CF₃. We are interested in the time evolution of the products and their energy distributions as well as in the pure rotational spectrum of the CF₃ radical. Marty will continue with the spectroscopy of this system this fall in collaboration with Nancy Triggs.

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