

AD-A171 904

THE SPECTROSCOPY AND REACTION KINETICS OF TRANSIENT
SPECIES(U) NORTHWESTERN UNIV EVANSTON IL DEPT OF
CHEMISTRY E WEITZ 04 JUN 86 AFOSR-TR-86-8537

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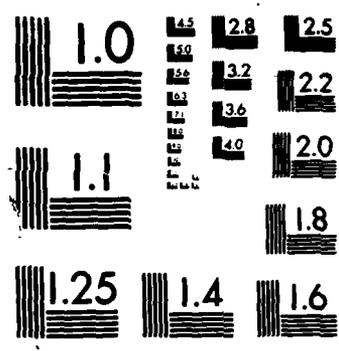
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SECURITY CLASSIFICATION OF THIS PAGE

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REPORT DOCUMENTATION PAGE

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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		A	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR. 86-0557	
6a. NAME OF PERFORMING ORGANIZATION Northwestern University	6b. OFFICE SYMBOL <i>(If applicable)</i>	7a. NAME OF MONITORING ORGANIZATION AFOSR	
6c. ADDRESS (City, State and ZIP Code) Department of Chemistry Evanston, IL 60201		7b. ADDRESS (City, State and ZIP Code) Building 410 Bolling AFB, Washington D.C. 20332	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR/NE	8b. OFFICE SYMBOL <i>(If applicable)</i>	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-85-0099	
8c. ADDRESS (City, State and ZIP Code) Building 410 Bolling AFB, Washington D.C. 20332		10. SOURCE OF FUNDING NOS.	
		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2917
		TASK NO. A3	WORK UNIT NO.
11. TITLE (Include Security Classification) The Spectroscopy and Reaction Kinetics of Transient Species			
12. PERSONAL AUTHOR(S) Eric Weitz			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 1/1/85 TO 12/31/85	14. DATE OF REPORT (Yr., Mo., Day) 6/4/86	15. PAGE COUNT 8
16. SUPPLEMENTARY NOTATION			

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A diode laser system has been acquired through the DoD-University Research Program. This diode laser system will be employed in an apparatus which will be used for studying transient gas phase species via IR spectroscopy. The apparatus has a time response of 35 nsec and a sensitivity of 10^{10} molecules/cc. The apparatus is capable of providing information on the structure, rates of reaction and rates of relaxation of transient species. It is currently being used to study reactions of vinyl radicals and energy disposition in CO's photoejected from metal carbonyl molecules.

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL My Joseph W Hager		22b. TELEPHONE NUMBER 202-767-4933	22c. OFFICE SYMBOL AFOSR/NE

DD FORM 1473, 83 APR

EDITION OF JAN 73 IS OBSOLETE 86-064

SECURITY CLASSIFICATION OF THIS PAGE

AD-A171 904

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The Spectroscopy and Reaction Kinetics of Transient Species

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This report represents the Final Technical Report for an equipment grant from the Department of Defense -University Research Instrumentation Program (FY 1984/FY 1985) administered by the Air Force Office of Scientific Research.

This grant provided for the acquisition of a diode laser system which has greatly expanded the ability of the principal investigator to conduct research involving the detection and monitoring of transient gas phase species. Included in the general types of species to be investigated with this system are coordinatively unsaturated organometallic compounds, organic radicals and neutral, saturated molecules. The mode of investigation involves transient infrared spectroscopy with the details of the experimental procedure have been delineated in references 1-7. A brief description of the apparatus (shown in figure 1) follows. The excimer laser produces the transient species to be studied via UV photolysis of an appropriate precursor molecule. The probe laser, in this case the diode laser, is incident on the photolysis cell and counterpropagates with respect to the excimer

laser. The diode laser is incident on an infrared detector which senses changes in the amplitude of the diode laser beam due to absorption produced by the transient species. These absorptions cause a transient change in the light intensity incident on the detector which is converted into a time versus intensity trace. This trace is captured via a transient digitizer and fed to a computer which stores this signal along with signals taken at other diode laser frequencies. When signals have been acquired over an appropriate frequency range, the computer is instructed to assemble a transient spectrum by connecting points at a common delay time from each transient. This produces an infrared spectrum at a given delay time over the frequency range that has been probed by the diode laser. This procedure can be repeated to assemble spectra at different delay times which allows one to observe the change in the IR spectrum due to reaction or relaxation of the transient species. Since IR spectra are highly structure specific, this, in turn, allows one to obtain information on the structure of the transient species^{1,6,7}. From the rate of decay of the transient, rate constants can be obtained for reaction of the transient with appropriate added gases¹⁻⁷. In addition, it has been shown to be possible to obtain information on the disposition of energy in the internal degrees of freedom of the transient species and on the rate of relaxation of the transient species^{3,6,7}. Thus, clearly the diode laser system provides us with a high degree of versatility which allows us to obtain valuable and unique information on the structure and reaction kinetics of a variety of transient species.

The diode laser system, which was purchased from the Laser Analytics Division of Spectra Physics Corp., provides continuously tunable radiation from 500-2400 cm^{-1} and from 2900-3300 cm^{-1} . This spectral range overlaps the absorptions of virtually all transient species of interest. In addition to the diode lasers, the laser system includes a mounting head and associated electronics which provides for temperature and current control of the lasers, a monochromator which allows for the determination of the operating frequency of the diodes, appropriate infrared detectors, two of which (an InSb and a Au:Ge) were purchased from Santa Barbara Research Corp, and a Computer system which is used for data acquisition and analysis. This computer system is based on an IBM PC-AT system which was purchased from Inacomp Corp. The total cost of the entire diode laser system was \$93,385.

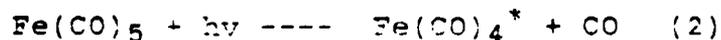
Acquisition of the essential components of the diode laser system was completed in November of 1986 with the delivery of the last set of diode lasers. Since that time we have been involved with set-up and initial experiments. We are currently actively engaged in two projects involving the diode laser system. In one project we are looking at the reaction of vinyl radicals with various H atom and halogen atom donors⁸. The vinyl radicals are produced via UV laser photolysis of vinyl bromide which is synthesized in-house. Once produced the vinyl radicals, which are very important species in combustion processes, are allowed to react with, for example, HCl or H₂ and the reaction is monitored via a change in absorption of a diode laser tuned to an absorp-

tion of ethylene, a product of the reaction as shown below in equation (1). These studies will allow us to measure the rate



constants for reaction of the vinyl radical with a variety of hydrocarbon species. These rate constants are necessary for modeling of combustion processes. Since neither the vinyl radical or the typical reaction product have conveniently accessible UV absorption spectra it is very difficult to monitor the reactions of this radical by any means other than transient IR spectroscopy. Once these initial studies are complete, we hope to obtain spectral information on the vinyl radical itself. This data will be invaluable for obtaining precise information on the structure of the radical.

The other project we are working on involves obtaining information on energy disposition in CO produced via excimer laser photolysis of various metal carbonyls⁹. We have postulated that the gas phase photodissociation of metal carbonyls involves an initial loss of one CO molecule and the production of a coordinatively unsaturated fragment with a high degree of internal excitation^{6,7}. This is illustrated schematically in equation (2).



If the coordinatively unsaturated fragment contains sufficient internal energy it can continue to lose CO's in a RRKM type

process until the internal energy content is sufficiently low that further dissociation is improbable.^{6,7} Since each CO that is lost comes from a parent with a very different internal energy distribution, the CO should be produced with different internal energy distributions. Thus by monitoring the CO internal energy states with a diode laser it should be possible to determine if this dissociation mechanism is indeed the operative mechanism. In addition, we have postulated that certain excited electronic states of coordinatively unsaturated photofragments are intermediates in some of the photodissociation processes in these systems. This should also be definitively ascertainable via the experiments currently in progress. When completed this work will provide a much more definitive picture regarding the dissociation dynamics of metal carbonyls than currently exists. This will allow for the prediction of rates of production of the various coordinatively unsaturated photofragments from a given parent. This in turn will establish a maximum rate for reaction of the coordinatively unsaturated fragments since they obviously cannot react until they are produced.

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