

UNCLASSIFIED

DTIC FILE COPY

2

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR. 89-1858	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Acquisition of Laser and Signal Processing Equipment		5. TYPE OF REPORT & PERIOD COVERED Final 4/83 - 3/84
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) E. R. Grant P. L. Houston J. R. Wiesenfeld		8. CONTRACT OR GRANT NUMBER(s) AFOSR-83-0279
9. PERFORMING ORGANIZATION NAME AND ADDRESS Cornell University Ithaca, New York 14853		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research Bolling Air Force Base, D.C. 20332		12. REPORT DATE January 10, 1985
		13. NUMBER OF PAGES 13
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This release:		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		

DTIC
ELECTE
JAN 4 1990
S B D

90 01 04 189

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD-A216 821

State-of-the-art laser and signal processing equipment have been purchased to aid ongoing projects of interest to the Department of Defense. Two EMG 150-ES-C high-power excimer lasers and three FL2002E dye lasers have been assembled into a tunable vacuum ultraviolet laser system and a high-power, high-resolution tunable laser resource. In addition, a new computer-based data acquisition system has been assembled and tested; it allows much more flexible analysis of the data in addition to higher storage capacity. Cornell University has shared the costs of the new facility by supporting an extensive remodelling of the laser laboratory.

The instruments are being used in four DoD-sponsored programs: Edward R. Grant has used the high-power, high-resolution resource to study fragmentation dynamics of energetic materials, especially the primary decomposition processes for nitro-paraffins and nitramines (sponsored by ARO). Paul L. Houston has used the tunable vacuum ultraviolet system in his studies of halogens and oxygen (AFOSR) and in investigations of the interactions of vibrationally excited molecules with solid surfaces (ARO). John R. Wiesenfeld has used the laser systems in studies of energy storage and transfer in gas lasers (AFOSR).

Brief descriptions of the tunable vacuum ultraviolet laser; the high-power, high-resolution tunable laser; and the computer acquisition/analysis system follow.



☒	
☐	
☐	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Tunable Vacuum Ultraviolet Laser System

A four-wave mixing technique using magnesium vapor has been used to provide tunable radiation in the 140-160 nm region.

Two photons from one of the excimer-pumped dye laser are used to populate the 3s3d level in Mg, while a second, tunable photon derived from the other excimer-pumped dye laser is used to stimulate Raman gain in the vacuum ultraviolet. The output frequency at $\omega = 2\omega_1 + \omega_2$ has been demonstrated by sensitively detecting CO using laser-induced fluorescence on the A+X transition. A spectrum of room-temperature CO at 10^{-6} torr is shown in Fig. 2B of the attached preprint.

We have recently used these techniques to study the photodissociations of glyoxal, as described in detail in the preprint, and of OCS, described briefly here. A KrCl excimer laser at 222-nm was used to dissociate OCS in a molecular beam, while our tunable vacuum ultraviolet laser was used to probe the CO and sulfur products by laser-induced fluorescence. The results show that both $S(^3P)$ and $S(^1D)$ are produced, that all of the CO is formed in its lowest vibrational level, and that the CO(v=0) rotational distribution is extremely inverted; the rotational levels have roughly a Gaussian distribution centered at J=57. When higher backing pressures of OCS are used in the nozzle source, we can also observe the dissociation of an OCS dimer or polymer. The product CO in this case is characterized by a Boltzmann-like distribution of rotational population corresponding to a temperature of 50 K. The results for the OCS monomer are reasonable in light of previous experiments which suggest

P
24
X

X

that the excited state is bent. Theoretical modeling of the dissociation dynamics is in progress and should give some indication of the bond angle in the excited state.

High-power, High Resolution Tunable Laser Resource

Radiation from the second excimer laser pumps the third dye laser to yield intense output pulses tunable from 220 to 850 nm. This light is used as a source for the nonlinear spectroscopic detection of unimolecular fragmentation products of energetic materials. The specific technique most often employed is ultra-sensitive two-photon resonant three-photon ionization. By virtue of the two-photon resonance structure we obtain information on product rovibrational distributions that reflect the internal state dynamics of the decomposition. These decompositions are carried out within a skimmed molecular beam, and the spatial and temporal resolution of our focussed laser probe gives in addition information on fragment recoil velocity distributions.

In support of these investigations we have worked to find new two-photon transition systems which can be used to characterize energetic products. We have achieved greatest success with NO_2 , where we have found strong resonance enhancement in two-photon transitions to the sharp band systems of the $3p\sigma^2\ ^2\Sigma^+_u$ and $3p\pi^2\ ^2\Pi_u$ Rydberg states. A unique feature of these transitions is that intermediate resonance with a dense system of strongly mixed intermediate states dramatically widens the Franck-Condon envelope, making these resonances especially convenient for product state characterization.



Computer Based Signal Processing Equipment

As part of the equipment acquisition program, we have opted for the purchase of a microcomputer to assist in data collection and experimental control. Although we have previously standardized on the LSI 11/xx family, the inherent limitations on "live" memory (to 64kB) and the relatively high cost of these systems suggested that alternatives should be considered. Accordingly, we purchased an IBM XT with 512 kB of memory, a color graphics board, monochrome monitor and a Data Translation Interface which affords up to sixteen channels of A/D input, two channels of D/A output and sixteen lines of digital I/O. In addition, we purchased the ASYST software package to permit efficient realtime data acquisition, analysis and display. The time saving (in excess of three man-months) greatly outweighed the cost of the software package (\$1395).



APPENDIX

STATE-TO-STATE PHOTOCHEMISTRY OF GLYOXAL USING A TUNABLE VUV LASER FOR PRODUCT DETECTION

John W. Hepburn

Centre for Molecular Beams and Laser Chemistry
Department of Chemistry
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

and

N. Sivakumar and P. L. Houston
Department of Chemistry
Cornell University
Ithaca, New York, U. S. A. 14853

ABSTRACT

The predissociation of glyoxal has been studied by laser excitation of glyoxal molecules in a supersonic beam, followed by VUV laser-induced fluorescence (LIF) detection of the photofragments. Preliminary results on the time evolution of the photodissociation, as well as the internal energy distribution of the CO photoproduct will be discussed.

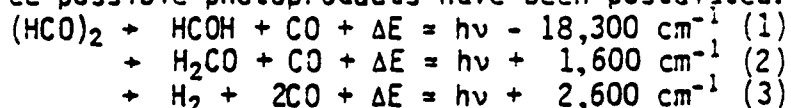
INTRODUCTION

In recent years there has been a surge of interest in learning how the initial state of a reactant affects the products in a chemical process. Knowledge of the state-to-state relationship between reactants and products not only allows practical control of reactions but often leads to a detailed understanding of the potential energy surfaces on which they occur. To date, however, there have been only a few systems on which state-to-state chemistry has been possible. One of the most convenient of these is a molecule undergoing predissociation. Since a predissociating molecule often possesses a structured absorption, state-selected excitation can easily be achieved. Furthermore, the unimolecular nature of the dissociation process makes it possible to determine the probability for formation of product states under isolated-molecule conditions, where collisions have not disturbed the nascent populations. Several examples of the power of state-to-state photochemistry have recently appeared, including studies of van der Waals compounds,¹ CF_3NO ,^{2,3} and HONO .⁴ Most experiments, however, have been limited by the need to examine

photodissociations in which the product fragment(s) absorb light in the visible or near ultraviolet regions accessible by commercial lasers.

Recently, vacuum ultraviolet sources have greatly expanded the scope of state-to-state experiments, particularly those involving the CO molecule. Shortly following the report by Wallace and Zdasiuk of four-wave mixing in Mg vapor to produce tunable VUV wavelengths in the 150-nm region,⁵ several studies involving detection of products by VUV laser induced fluorescence near this wavelength appeared in the literature. Bromine atoms were detected as products of the $F + HBr$, $H + Br_2$ and $H + HBr$ reactions by resonance atomic fluorescence,⁶⁻⁸ while CO was detected by LIF on the $A^1\Pi + X^1\Sigma$ transition as the product of both scattering from solid surfaces⁹ and photodissociation of H_2CO .¹⁰ In this paper we report preliminary results on the elucidation of the state-to-state photodissociation dynamics of glyoxal using VUV laser induced fluorescence to detect the CO produced following selective excitation of glyoxal to individual vibronic levels of its first excited singlet state.

While both the spectroscopy and photophysics of the S_1 state of glyoxal have been extensively studied,¹¹ its photochemistry is not fully understood. Along with formaldehyde, glyoxal stands as an important test case for theories of unimolecular photodissociation. Until recently it was doubted that photochemistry took place at all from low vibronic states of S_1 in the absence of collisions.¹² It is still not known whether the dissociation is a prompt unimolecular event or whether there might be a long-lived intermediate.¹³⁻¹⁵ However, a recent molecular beam study carried out by one of the authors¹⁶ has demonstrated the presence of photochemistry in the absence of collisions and has provided detailed information on the branching ratios for different channels and on the microscopic fragmentation mechanism. Three possible photoproducts have been postulated:



The yield for each of these three channels is thought to be 7%, 65%, and 28%, respectively.¹⁶ From the large difference in available energy, particularly between channels (1) and (2), one might predict an interesting internal energy distribution in the CO product. One object of the current study was to determine that distribution. A second object was to measure the time dependent production of CO in order to confirm or disprove the presence of a long-lived intermediate in the collisionless dissociation.

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Fig. 1. The photolysis laser was an excimer-pumped dye laser (Lambda Physik 101, 2002) and was tuned to the 8^1 vibronic transition of glyoxal near 440.3 nm. The vacuum ultraviolet probe laser was similar to that described previously,⁵ with the exception that the dye lasers (each a Lambda Physik 2002) were

pumped by the two output beams of a dual cavity excimer laser (Lambda Physik 150ES). The two excimer pulses, derived from the same power supply, were locked in time to one another and separated by about 16 ns. By adjusting the optical delay caused by the two beam paths, the outputs of the dye lasers could be made to coincide temporally at the input of the magnesium heat pipe. The fixed frequency dye laser was made to operate at 430.9 nm, while the variable frequency dye laser scanned the range from 469.5-480 nm. The resulting VUV output in the range from 147.7-148.7nm was used to probe the (2,0) vibrational band of the CO A $\rightarrow$ X transition.

Glyoxal was seeded at 5% in helium and expanded through a pulsed valve of the design described by Adams et al.¹⁷ The molecular beam chamber has been described in detail elsewhere.¹⁸ The photolysis and probe laser beams were propagated collinearly in opposite directions and were perpendicular to the molecular beam. Fluorescence induced in glyoxal by the photolysis laser and fluorescence induced in CO by the VUV laser were collected in opposite directions, each mutually orthogonal to the laser and molecular beams. A Hamamatsu photomultiplier (R928) was used to detect the glyoxal fluorescence, while an EMR photomultiplier (S41G-09-17) was used to detect the CO fluorescence. A reflection from the exit window for the VUV laser was detected by a third photomultiplier (EMI; G-26-E314LF).

The signal from each photomultiplier was fed to a boxcar integrator (PAR 162 or Stanford Research Systems), while the outputs from each integrator was fed to one of three channels of an A/D converter. A computer (LSI 11/02) read the A/D converters and normalized the signal channel by dividing by voltages proportional to the VUV intensity and the glyoxal fluorescence. The normalized signal was plotted during each run and then stored for later analysis.

For some scans, one of the boxcars was operated in the active background subtraction mode. The photolysis laser was fired at half the repetition rate of the probe laser, and the boxcar was then made to average the difference between the signal with and without the photolysis laser. In this way, it was possible to correct the signal both for CO impurities in the glyoxal sample (which caused some interference in measuring low rotational levels of CO(v=0)) and for the possibility that the probe laser might itself dissociate some glyoxal and simultaneously excite the CO product. However, no evidence for the latter effect was observed.

The appearance rate of the CO photoproduct was measured by scanning the delay of the probe laser relative to the photolysis laser while keeping the boxcar gates for the CO fluorescence and VUV intensity locked to the probe laser.

Glyoxal was prepared from the trimer, obtained in 99% purity from sigma. The trimer was mixed thoroughly with P₂O₅ and heated to 160-180 °C. Water was trapped at -0°C, and the glyoxal monomer collected at liquid N₂ temperature. Immediately following

preparation, the glyoxal monomer was distilled from a bath at 0°C to one at -73°C. At the latter temperature, formaldehyde and CO have high vapor pressures, whereas glyoxal is trapped as a solid.

RESULTS

Figure 2a displays a spectrum of the CO photoproduct of glyoxal dissociation. In the wavelength region of this diagram, the VUV laser probes primarily CO($v=0$). For comparison, a spectrum of room temperature CO at a pressure of 2×10^{-6} torr is displayed in Fig. 2b. It is evident that, while the CO product of glyoxal dissociation is more rotationally excited than is a Boltzmann distribution at room temperature, it is not as highly excited as the CO distribution from formaldehyde dissociation.^{10,19} It is also clear that many more lines are present in the LIF spectrum of the CO photoproduct than in the spectrum of room temperature CO. Although a detailed analysis has not yet been performed, it is possible that these additional lines are due to absorption by vibrationally excited CO product molecules. For example, the (5,2) and (4,1) bands lie in the same spectral region.

The appearance time of the CO photoproduct is shown in Fig. 3. The risetime of the signal, about 1 μ sec, is equal within the experimental uncertainty to the decay time of fluorescence from the 8^1 level of glyoxal²⁰. The apparent decay of the signal in Fig. 3 is a result of the CO fragment leaving the viewing zone at the beam velocity ($\approx 1.4 \times 10^5$ cm/sec), which will take on the order of 2-4 μ sec, as observed.

DISCUSSION

The study of simple atom transfer reactions ($A+BC \rightarrow AB+C$) has shown that detailed knowledge of energy disposal in a chemical process can be translated into detailed knowledge of the potential energy hypersurface. Similarly, for a photofragmentation process, the detailed microscopic mechanism can be obtained from a thorough knowledge of the energy release in the fragmentation. As an example, the high level of rotational excitation of the CO product observed in H_2CO photodissociation indicates dissociation occurs through a very constrained, highly bent intermediate. The preliminary data for glyoxal seem to indicate the photodissociation process channels much less energy into rotation and instead energy is deposited into vibrational excitation. A detailed analysis of the CO photoproduct internal energy distribution, when combined with the data already available on translational energy in the products¹⁶ will provide a fairly complete picture of the dissociation mechanism. Such an analysis will be available soon, when a more thorough study has been completed.

Even though two other groups have suggested the presence of a slowly decaying intermediate in the photochemistry of glyoxal,¹²⁻¹⁵ the appearance time of CO displayed in Fig. 3 leaves little doubt that the collisionless photochemistry of glyoxal is prompt. The appearance time of the CO is in sensible agreement with the decay time of the 8^1 level of S_1 glyoxal (0.87 usec^{20}). The cause for the discrepancy between the previous results and those presented here is not yet clear.

Another result of this preliminary study is that it demonstrates the sensitivity of VUV laser-induced fluorescence for detection of CO photoproducts. Figure 2b shows that even with relatively little signal averaging (10 shots/point) the sensitivity for detection of CO is quite good. For these experiments, the CO detection limit was on the order of 10^7 molecules/cm³ in a given quantum state, and improvements to the apparatus can increase this sensitivity by 10-100 times.

CONCLUSIONS

The data presented in this paper, though preliminary, provide new information about the detailed mechanism for glyoxal predissociation. The possibility of doing state to state dissociation experiments on glyoxal has been demonstrated, and it has been clearly shown that collisionless glyoxal predissociation does not proceed through a long lived intermediate.

Much work remains to be performed on the photodissociation of glyoxal. Detailed calculations of the vibrational and rotational distributions have yet to be made. While the present work has concentrated on vibronic excitation of the 8^1 transition in glyoxal, several other vibrational states may readily be examined in order to determine how the CO vibrational and rotational distributions depend on the internal energy of the glyoxal parent compound. Indeed, it would even be possible to examine the dependence of the final states on the initial rotational level excited in glyoxal. Finally, a recent publication has reported that the triplet state of glyoxal can be populated directly by laser excitation in a molecular beam.²¹ It would be interesting to examine how the photochemistry from the individual levels of the triplet state differs from that of the singlet state.

It should be emphasized that the availability of VUV laser sources now opens up a wide range of experiments in molecular dynamics. In particular, the sensitive detection of CO demonstrated in this work should make it possible to examine in detail the dissociation mechanisms of several other aldehydes. Indeed, progress along these lines has been made concurrently with our work.¹⁹ Detection of CO produced in the photodissociation of other compounds such as OCS, CO₂ and HCO can readily be envisioned. Finally, since CO is a prominent species in many interesting dynamical processes, it is likely that other state-to-state experiments, such as translation to vibration/rotation energy transfer in atomic collisions with CO and molecular beam scattering studies involving CO, will shortly appear. The possibilities for extending similar VUV detection techniques to other molecules (such as H₂) are endless.

ACKNOWLEDGEMENTS

This work has been supported by a grant and a University Research Fellowship to JWH from NSERC and by the National Science Foundation through grant CHE-8314146 to PLH. Travel between Ontario and New York were provided by a NATO grant for international collaboration. The experiments were performed in the Facility for Laser Spectroscopy in the Department of Chemistry at Cornell University with lasers supplied by a DoD Instrumentation grant (AFOSR-83-0279). We are grateful to D. Bamford and C. B. Moore for communicating their results to us prior to publication.

REFERENCES

1. W. Sharfin, K. E. Johnson, L. Wharton, and D. H. Levy, J. Chem. Phys. 71, 1292 (1978).
2. R. W. Jones, R. D. Bower, and P. L. Houston, J. Chem. Phys. 76, 3339 (1982).
3. R. D. Bower, R. W. Jones, and P. L. Houston, J. Chem. Phys. 79, 2799 (1983).
4. R. Vasudev, R. N. Zare, and R. N. Dixon, Chem. Phys. Lett. 96, 399 (1983); J. Chem. Phys., to be published.
5. S. C. Wallace and G. Zdasiuk, Appl. Phys. Lett. 28, 449 (1976).
6. J. W. Hepburn, D. Klimek, K. Liu, J. C. Polanyi, and S. C. Wallace, J. Chem. Phys. 69, 4311 (1978).
7. J. W. Hepburn, D. Klimek, K. Liu, R. G. Macdonald, F. J. Northrup, and J. C. Polanyi, J. Chem. Phys. 74, 6226 (1981).
8. J. W. Hepburn, K. Liu, R. G. Macdonald, F. J. Northrup, and J. C. Polanyi, J. Chem. Phys. 75, 3353 (1981).
9. J. W. Hepburn, F. J. Northrup, G. L. Ogram, J. M. Williamson and J. C. Polanyi, Chem. Phys. Lett. 85, 127 (1982).
10. P. Ho and A. V. Smith, Chem. Phys. Lett. 90, 407 (1982).
11. see Y. Osamura, H. F. Schaefer III, M. Dupuis, and W. A. Lester, Jr., J. Chem. Phys. 75, 5828 (1981) and references therein.
12. R. Naaman, D. M. Lubman, and R. N. Zare, J. Chem. Phys. 71, 4192 (1979) and references therein.
13. G. W. Loge, C. S. Parmenter, and B. F. Rordorf, Chem. Phys. Lett. 74, 309 (1980).
14. G. W. Loge and C. S. Parmenter, J. Phys. Chem. 85, 1653 (1981).
15. G. Loge and C. S. Parmenter. Abstract for the 14th Informal Conference on Photochemistry, March 1980.
16. J. W. Hepburn, R. J. Buss, L. J. Butler, and Y. T. Lee, J. Phys. Chem. 87, 3638 (1983).
17. T. E. Adams, B. H. Rockney, R. J. S. Morrison and E. R. Grant, Rev. Sci. Instrum., 52, 1469 (1981).
18. W. G. Hawkins and P. L. Houston, J. Chem. Phys. 86, 704 (1982).
19. D. Bamford and C. B. Moore, private communication.
20. B. G. MacDonald and E. K. C. Lee, J. Chem. Phys., 71, 5049 (1979).
21. L. H. Spangler, Y. Matsumoto, and D. W. Pratt, J. Phys. Chem., 87, 4781 (1983).

Figure 1

Schematic diagram of the photodissociation apparatus described in the text. The beam chamber is on the right of the diagram, with the molecular beam perpendicular to the plane shown.

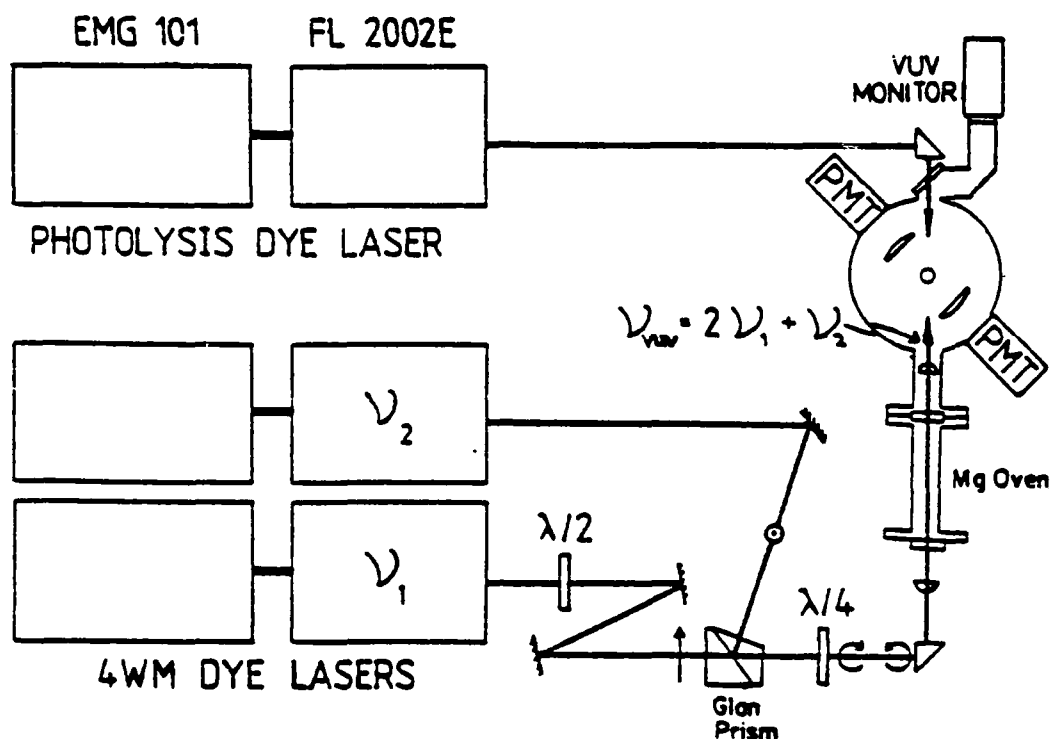


Figure 2

a) Spectrum of CO photoproduct from predissociation of the $\frac{1}{0}8$ band of glyoxal. The spectrum was recorded at 1 μ sec delay after the photolysis laser and is uncorrected for background CO.

b) Spectrum of 300K CO in a gas cell at a measured pressure of 2×10^{-6} torr.

In both cases, the wavelengths scale is the wavelength of the tunable dye laser (ν_2).

FIG. 2A

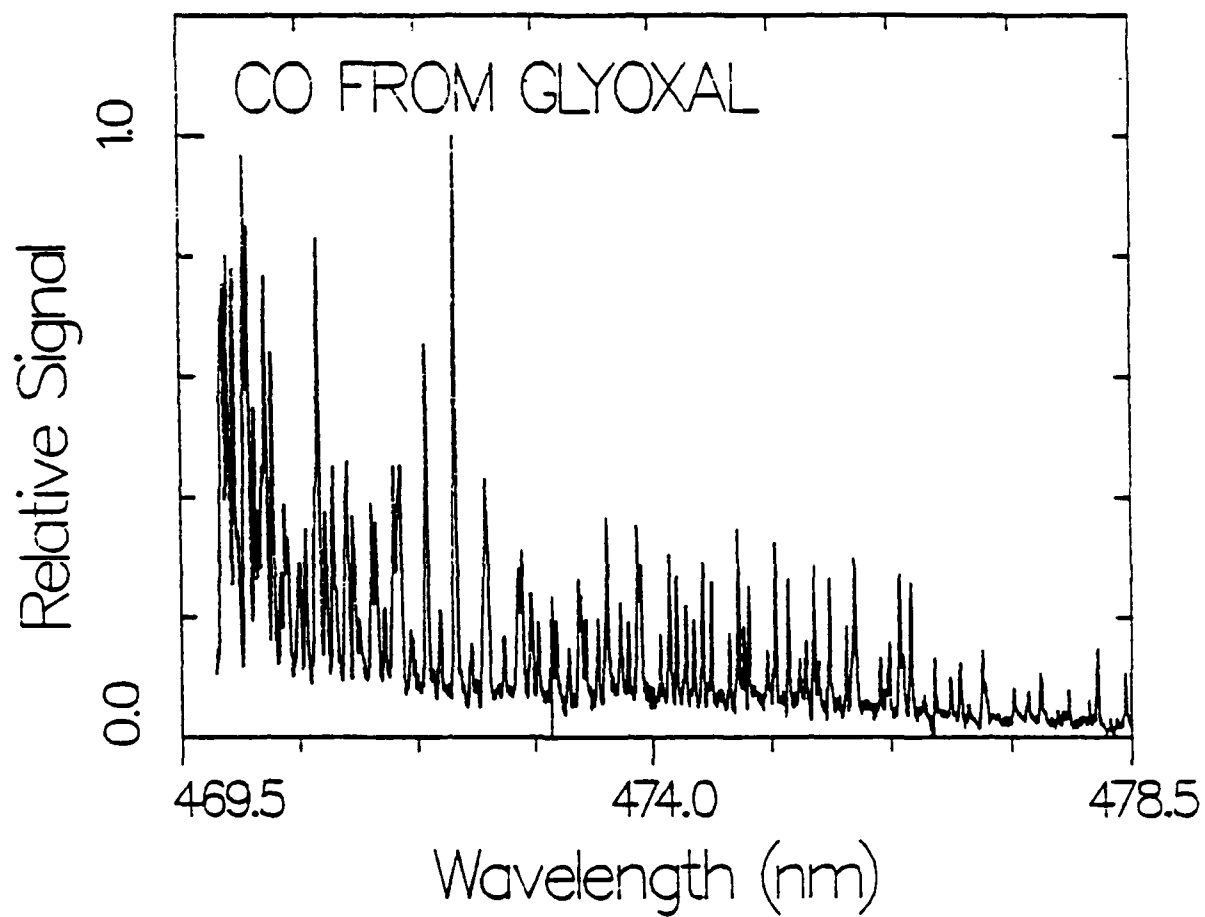


FIG. 2B

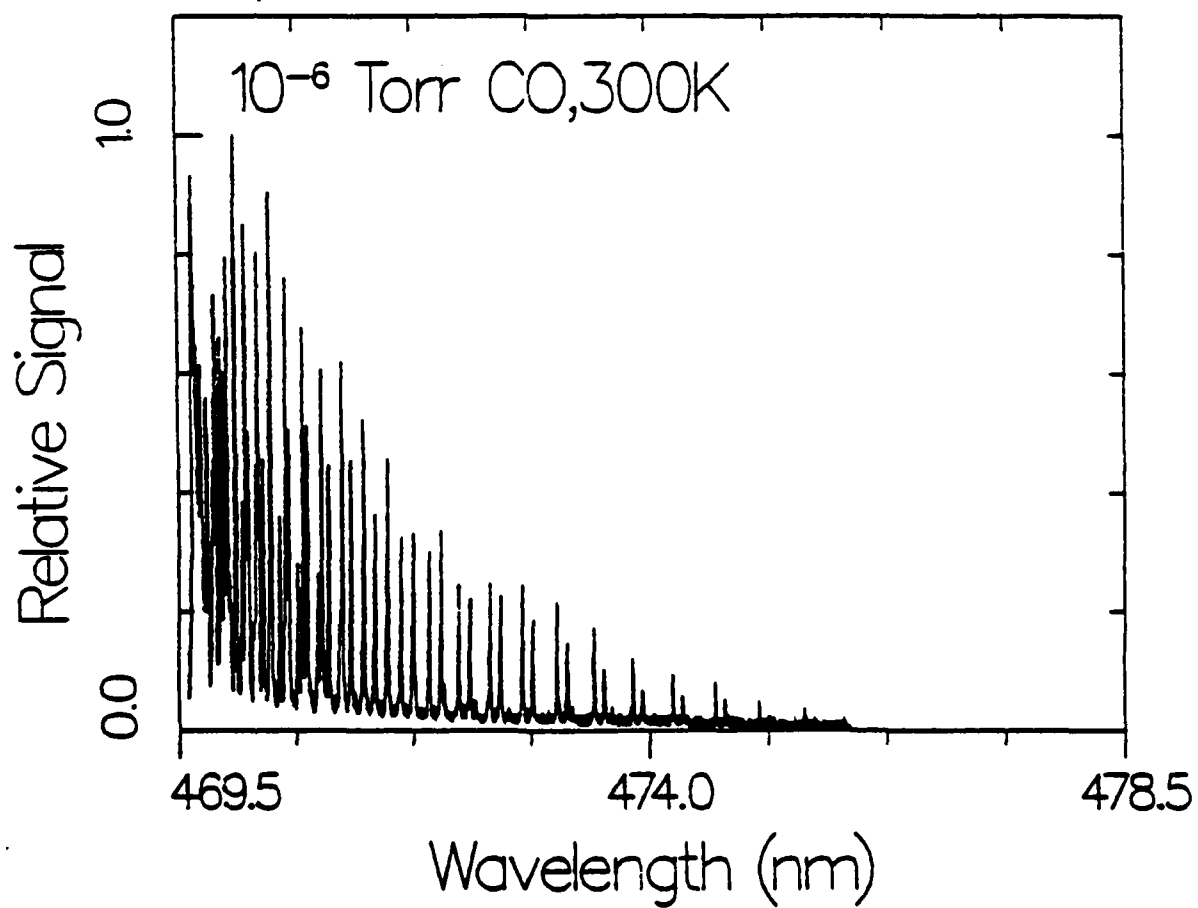


Figure 3

Time dependence of CO signal as a function of delay between VUV probe laser and photolysis laser. Oscillating structure on leading edge is rf interference from the photolysis laser.

