AD-A051 063 CALIFORNIA UNIV BERKELEY DEPT OF CHEMISTRY F/G 20/5
CHEMICAL LASERS AND LASER-INDUCED KINETIC PROCESSES.(U)
SEP 77 G C PIMENTEL AFOSR-74-2616
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(18) **REPORT DOCUMENTATION PAGE** (9)

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. ~~REPORT NUMBER~~ AFOSR-TR- 78 - 0207

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER (9)

4. ~~TITLE (and Subtitle)~~ (6) CHEMICAL LASERS AND LASER-INDUCED KINETIC PROCESSES. (2)

5. ~~TYPE OF REPORT & PERIOD~~ COVERED Final rept. 1 Oct 74 - 30 Sep 77,

6. PERFORMING ORG. REPORT NUMBER

7. ~~AUTHOR(s)~~ (10) George C. Pimentel

8. ~~CONTRACT OR GRANT NUMBER(s)~~ (15) AFOSR-74-2616 new

9. PERFORMING ORGANIZATION NAME AND ADDRESS
University of California, Berkeley
Department of Chemistry
Berkeley, California

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
61102F
(16) 2303 B1 (17)

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Office of Scientific Research/NC
Bolling AFB DC 20332

12. ~~REPORT DATE~~ (11) 30 Sep 77

13. NUMBER OF PAGES ~~20~~ (12) 22 p.

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)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

DDC
MAR 10 1978
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Chemical laser
Intracavity spectroscopy
Photolysis
Cryogenic thermoluminescence

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

The 'tandem-laser' and 'zero-gain' methods have been used to study the primitive vibrational populations obtained in selected chemical reactions. The photolysis of HN_3 in the presence of fluorinated methanes and argon produces HF through NH insertion-elimination reactions, but chemical laser emission has not been observed. The HF vibrational population ratios were measured from 225 to 400 K for CF_4, CF_3H, CF_2H_2, and CFH_3. Photolysis of hexafluoroacetyl acetone was found to produce HF in a primary reaction involving elimination of HF and ring closure. This new type of HF photoelimination reaction does not require vacuum ultraviolet

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20. Abstract (continued)

wavelengths. ClF, ClF_3 and ClF_5 photolyzed with H_2 result in high-gain HF and HCl lasers with emission from high rotational quantum numbers. The mechanism proposed involves both V-V and V-R energy transfer which causes vibrational excitation to pool in high J states where equilibration is slow. Such a process limits the efficiency and wavelength of all HF chemical lasers. Pure rotational laser emission in difluoroethylene photoelimination is observed on transitions up to J = 30 to 29, the highest J transitions observed from chemical pumping of HF.

Shock tube pyrolysis of tetramethyl dioxetane resulted in light emission, indicating a possible chemically pumped electronic transition laser system. An intracavity dye laser spectroscopy (IDLS) investigation of the Ba + N_2O reaction shows gain on certain Ba transitions but only absorption in BaO. No positive gain from SnO in the corresponding Sn reaction was detected. Transitions from excited Sr atoms were abserved in IDLS experiments, demonstrating the applicability of IDLS to excited states spectroscopy. Inconclusive results were found in HF(v=4,3,...) + D_2 exchange reactions. Photolysis of ethylene with O_2 showed HCO absorptions at 614nm. In formaldehyde photolysis HCO was detected and its reaction rate constants with O_2 and NO were measured.

Cryogenic thermoluminescence of photolyzed N_2O in Ar was seen in the Herzberg bands of O_2. Photolysis of OCS in various matrices yielded S_2 thermoluminescence from three bands, two of which had never been detected before. Cryogenic thermoluminescence from SO_2, SO, and other reaction products has also been detected.

AFOSR-TR- 78 - 0207

Final Report
to the
Air Force Office of Scientific Research

Chemical Lasers and Laser-Induced Kinetic Processes

Grant #AFOSR-74-2616-ABC

October 1, 1974 - September 30, 1977

This report describes research accomplishments over the period October 1, 1974 to September 30, 1977.

George C. Pimentel
Professor of Chemistry
Principal Investigator

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Research Accomplishments

Research Accomplishments

I. Vibration-Rotation Chemical Lasers

~~During the grant period, we have exploited~~ the "Tandem Laser" and "Zero Gain" methods (developed in these laboratories) to study the primative vibrational populations obtained in selected chemical reactions HAVE BEEN EXPLOITED. The NH-fluoromethane insertion-elimination reactions were carefully examined as a prototype example of this type of chemical laser. Then, intensive study was devoted to the ClF_x-H_2 chemical lasers (x=1, 3, 5) because of the likelihood that chain branching might be involved and because of the special information they provide about the role of rotational degrees of freedom and energy-transfer processes.

NH-Fluoromethane Insertion-Elimination Chemical Lasers (ref. 1,6)

Hydrohalide photoelimination reactions characteristically place only a small fraction of the available energy into the hydrohalide vibrational degree of freedom. We wished to explore this question with a chemical elimination, using the tandem laser technique to permit quantitative measurement of the vibrational population ratios, even when population inversions are too low to reach laser threshold. We selected the insertion-elimination reaction, imine plus fluoromethane to give hydrofluoric acid and the appropriate imine.

$$NH(a\ ^1\Delta) + CH_xF_{4-x} \rightarrow HF(v) + CH_{x-2}F_{4-x}NH$$

e.g., for x=1

$$NH + CH_2F_3 \rightarrow HF + CF_2 = NH$$

The photolysis of hydrazoic acid, HN_3, in the presence of fluorinated methanes and argon produces hydrofluoric acid, HF, through imine (NH, probably a $^1\Delta$) insertion-elimination reactions, but chemical laser emission has not been observed. Nevertheless, by the tandem laser, zero-gain temperature method, the HF vibrational population ratios have been measured as a function of temperature (225-400°K) for CF_4, CF_3H, CF_2H_2, and CFH_3. Part of the HF is evidently produced by NH(a $^1\Delta$) insertion into the C-H bond with subsequent HF elimination. However, there is an unexpected, competing reaction that involves the C-F bonds, either NH insertion-elimination or hot H atom abstraction to form HF. The HF produced from CF_4 shows a simple, Arrhenius type temperature dependence fitted by the expression $N_1/N_o = 0.115 \exp(950 \text{ cal}/RT)$. The N_1/N_o ratios for CF_3H and CF_2H_2 can be correlated with those of CF_4 by assuming competing C-F and C-H bond reactions weighted by the relative number of each type of bond. With this interpretation, the C-H bond insertion-elimination produces HF with the temperature dependence $N_1/N_o = 1.52 \exp(-1240 \text{ cal}/RT)$. Consistent with all earlier chemical lasers based upon elimination reactions, both the N_2/N_1 and N_1/N_o ratios are below unity. At room temperature, the NH insertion into the C-H bond gives $N_1/N_o = 0.2$, the lowest population ratio yet measured for an elimination reaction and apparently HF(v=0) is produced with a lower activation energy than that for HF(v=1).

<u>Photoelimination of HF by Hexafluoroacetyl Acetone</u> (ref. 8)

Chemical product analysis by Bassett and Whittle* had led them to postulate the photolysis of 1,1,1,5,5,5 hexafluoracetylacetone (HFAA) resulted in ring closure to a cyclic dihydrofuranone.

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*J. Bassett and E. Whittle, Int. J. Chem. Kinet. 8, 857 (1976).

This unusual ring closure implies HF elimination, though HF could not be detected in their studies because of its chemical reactivity.

The sensitivity and alacrity of the tandem laser techniques were exploited to investigate whether, indeed, HF elimination was a primary process. Driver chemical lasers were selected to permit investigation of the effect of HFAA photolysis on the gain of HF transitions $P_1(4)$, $P_2(4)$, and $P_2(5)$. The delays and quenching that occurred proved beyond question that photolysis of HFAA produces HF in a primary reaction. Furthermore, the pressure dependence of the delays on the various transitions shows that the vibrational population ratio $N(v=1)/N(v=o) = N_1/N_o$ must be much less that 0.45 while the ratio N_2/N_1 is somewhat less than 0.3.

This study confirms, then, a rather unusual photochemical reaction. The HFAA exists in the enol form and, presumably, the carbonyl group provides the chromophore. Presumably, in the electronically excited state, the hydrogen bond that stabilizes the enol form is broken, permitting internal rotation into a conformation in which the OH and the opposite CF_3 group come into proximity. Elimination of HF and ring closure occurs.

Thus this work reveals new type of HF photoelimination reaction that does not require vacuum ultraviolet wavelengths and it demonstrates the utility and sensitivity of the tandem laser technique.

<u>ClF_x-H_2 Chemical Lasers (x=1,3,5)</u> (refs. 3,11,12)

All of the ClF_x-H_2 systems (x=1,3,5) emit both HCl and HF vibration-rotation laser emission and with durations extending long after photolytic pumping had ceased. The behavior suggests that chain-branching might be involved and, in any event, chain reactions cause these chlorinefluorides to be among the highest gain chemically pumped HF and HCl lasers. Of special interest has been the emission observed from relatively high rotational quantum numbers.

For example, HF vibration-rotation laser emission has been observed using a grating-selective cavity up to $P_1(20)$, $P_2(16)$, and $P_3(7)$ for the ClF_5-H_2 system. The upper states in these transitions reach the thermodynamic limit when vibrational and rotational energies are added. The ClF-H_2 system, again with grating selective cavity, emits in HF transitions $P_1(15)$, $P_2(16)$, and $P_3(8)$. The patterns of emission indicate that direct population of the high J states by the vibrational pumping reaction(s) can be ruled out. Neither is the behavior consistent with Boltzmann equilibration. Late threshold times and extended durations point to an energy transfer mechanism that involves rapid $V\rightarrow R$ deactivation with large ΔJ coupled with $V\rightarrow V$ pumping in $HF^{\ddagger}$-$HF^{\ddagger}$ collisions to give a cumulative increase in rotational energy. Thus $V\rightarrow V$ and $V\rightarrow R$ processes divert vibrational excitation into rotational excitation where it will tend to "pool" in high J states for which rotational equilibration is a slow process. Such energy transfer processes and pooling has not been recognized earlier, though it could be a significant factor in the efficiency and spectral composition of chemical laser emission in all HF chemical lasers.

II. Rotational Lasers (refs. 2,5,19)

The focus of attention has been on two rotational laser systems:

$$\begin{aligned} ClF + h\nu &\rightarrow Cl + F \\ F + H_2 &\rightarrow HF^{\ddagger} + H \\ H + ClF &\rightarrow HCl^{\ddagger} + F \\ &\rightarrow HF^{\ddagger} + Cl \end{aligned}$$

and

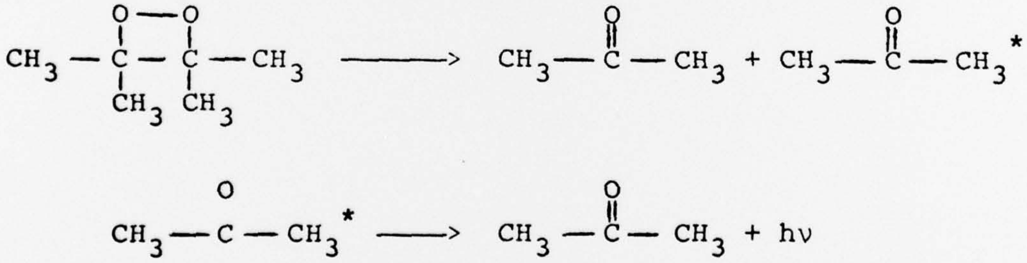
$$CH_2 = CF_2 + h\nu \rightarrow HC \equiv CF + HF^{\ddagger}$$

Both of these chemical systems emit HF rotational laser emission in the 10 to 20μ spectral region. For example, with rather large pressures, 80-100 torr of rather concentrated mixtures, $ClF:H_2:Ar = 1:1:10$, laser emission is seen in the spectral region 985-810 cm^{-1} with extremely long durations, up to 70 μsec. This corresponds to HF rotational transitions $J=22 \rightarrow 21$ and $J=24 \rightarrow 23$. The available energy in the $F + H_2$ reaction, 33 kcal/mole, is insufficient to populate the $v=0$, $J=22$ state, which requires 38 kcal/mole.

The photoelimination from 1, 1-difluoroethylene has continued to be of interest because of the high frequencies observed in the long wavelength region. Lines have now been detected in the spectral region 900 to 1050 cm^{-1}. Since this region includes the most intense emissions from a CO_2 laser, we have conducted CO_2-additive studies to verify that the emissions in question do not come from $HF^{\ddagger}$ vibration transfer pumping of impurity CO_2. With that possibility eliminated, we favor identification of these laser transitions as HF pure rotational transitions in the range J=25→24 up to J=30→29. These would be, to our knowledge, the highest J transitions observed from chemical pumping of HF. Of course, the photoelimination laser has a plethora of energy since relatively little is lodged in HF vibration. Nevertheless, the manner in which this much energy (40-50 kcal/mole) becomes concentrated in the rotational degree of freedom is a matter of great interest. The threshold times are short, about one μsec, so relatively few collisions are available for energy transfer processes: about 100 $HF-CH_2=CF_2$ collisions and at most a few HF-HF collisions. Consequently primitive distributions may be involved.

III. Electronic Lasers

Dioxetane Chemiluminescence (ref. 1): It is well known that the cyclic peroxides called dioxetanes decompose thermally in a chemiluminescent reaction. For example, for the tetramethyl dioxetane, the reaction is:



$$CH_3-\underset{CH_3}{\overset{O-}{C}}-\underset{CH_3}{\overset{-O}{C}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3^*$$

$$CH_3-\overset{O}{C}-CH_3^* \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + h\nu$$

Two methods were attempted to induce pyrolysis of this compound on a time scale sufficiently short to permit a substantial population inversion.[1] In the first method, the dioxetane was mixed with a hydrogen-chlorine mixture and the H_2-Cl_2 explosion was initiated through flash photolysis. It was hoped that the sudden temperature rise would rapidly pyrolyze the dioxetane and produce a substantial flash of visible light, signalling a propitious opportunity to achieve a chemically pumped electronic laser. This experiment was not promising. Severe decomposition occurred, suggesting that the chain carriers in the H_2-Cl_2 explosion were reacting with and consuming the parent dioxetane.

The second approach was based upon shock tube heating.[1] A shock tube was constructed with window ports placed a few centimeters from the reflector end of the shock tube. Helium driver was introduced throughout the shock tube, with a suitable pressure differential across the aluminum foil diaphragm. Just before operation, a few torr of detramethyldioxetane was introduced near the reflector end of the shock tube. Then the diaphragm was ruptured as an oscilloscope trace was triggered, recording the detector signal of a phototube viewing a narrow cross section of the shock tube contents through the viewing ports. Experiments with and without the dioxetane and with and without suitable filters verified that dioxetane pyrolysis and light emission was taking place as the reflected shock wave passed the viewing port the second time. This work, though promising, was terminated because Dr. Poole's commitment to a postdoctoral appointment required that he leave Berkeley. It is plain that the dioxetanes offer a significant opportunity for producing a chemically pumped electronic laser. Clearly, the optimum technique for rapid heating would be through pulse heating of a dioxetane-absorber gas with a pulsed, high energy, CO_2 laser. A suitable (and inert) absorber would be SF_6. Unfortunately, at the time these experiments were performed, we had no access to a high power CO_2 laser.

(It should be noted that both the synthesis and the handling of the dioxetanes are dangerous laboratory operations. Suitable explosion precautions should always be in effect).

Intracavity Dye Laser Spectroscopy: A Gain Probing Technique (ref. 4, 10).

In the Berkeley laboratory, the search for new, low-gain population inversions was significantly aided by our development of the "tandem laser" technique.* It was decided that the same gain-probe sensitivity could be used to search for chemically pumped electronic population inversion using a dye laser as the driver laser. As this method has been explored and applied, we have come to call it "Intracavity Dye Laser Spectroscopy", or IDLS.

A flashlamp-pumped dye laser was constructed based upon a 6 to 100 joule flash with a 1 μsec time to peak intensity. A suitable dye was selected to fit the spectral region in which possible absorption or emission might occur. Various chemical reactions and potential gain media were placed in the cavity to see their effect on the dye laser continuum. The dye laser output was focused onto the slit of a Jarrel-Ash 1-m grating spectrograph and the dispersed spectrum photographed on suitable emulsions. (For experimental details, see reference 4).

The earliest experiments were designed to verify the sensitivity of the technique as a population probe.[10] For example, with a

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*M. Molina and G. C. Pimentel, J. Chem. Phys. **50**, 3988 (1972).

flashlamp-pumped ruby rod in the cavity, the ruby flashed alone would reach laser threshold at 1800-2000 joules. With the dye laser also in the cavity, the entire dye laser output would become locked onto the 6943 Å ruby transition even when the ruby was pumped at energies of 1400 joules, for below the ruby threshold. Thus, the dye laser clearly signalled the ruby population inversion long before the ruby gain was sufficient to produce laser emission without support. This experiment demonstrated the efficacy of the IDLS method as a gain probe.

In the next experiment, a helium-neon discharge tube was placed in the dye laser cavity with the expectation that the helium-neon population inversion at 6328 Å would be readily detected with the enhancement by the dye laser emission. This effect was indeed obtained, but the experiments revealed unexpected and complicating behavior in the spectral neighborhood of absorbing transitions. This behavior could include apparent enhancements, suggestive of population inversions, immediately adjacent to a real absorption. The effects were not perfectly reproducibly and were traced to lensing effects associated with the anomalous dispersion associated with an absorption.

Applications of IDLS (ref. 4) Quite a number of chemical systems were investigated using this intracavity sensitivity either as a gain probe or in absorption.

1. Ba + N_2O (ref. 13). The research group of D. J. Ekstrom at Stanford Research Institute had constructed (with AFOSR support) a large barium oven and flow reactor with which to investigate the popular electronic laser candidate,

$$Ba(g) + N_2O(g) \rightarrow BaO^* + N_2$$

Upon hearing of our gain-probe technique, they invited us to bring our apparatus to Palo Alto to use with their reactor. J. P. Reilly moved our dye laser system to the SRI laboratories and conducted a number of collaborative studies. Gain on certain barium atomic transitions was detected but only absorption in the BaO transitions.

2. $Sn(^3P) + N_2O \rightarrow Sn\ O^* + N_2$ (ref. 4). Vapor phase Sn atoms were generated through flash photolysis of tin tetramethyl, $Sn(CH_3)_4$. With 1 torr of $Sn(CH_3)_4$, and about 10 torr N_2O, the dye laser spectrum showed a series of weak, complex, and closely spaced absorption frequencies in the spectral region 4900-5050 Å. Wavelength measurements permitted positive identification of well-known SnO absorption band heads; e.g.,

4836.4 Å	(3,8)	C↔X
4876.6 Å	(4,9)	C←X
4857.5 Å	(2.6)	B←X
4950.0 Å	(0,5)	B←X

No positive gain was detected, so evidently there is more SnO in the ground state than in either excited state, despite obvious chemiluminescence.

3. <u>Strontium Atom</u> (ref. 4). In this experiment, a heated cell containing strontium vapor was placed in the dye laser cavity. It was intended to attempt to observe upper stage electronic absorption from an electronic state populated by the photon flux in the dye laser cavity. The Sr atom was selected

because it has two known transitions involving the ground state and two excited states with spacings within 100 Å so that a single dye laser would span them both. The two transitions in question are

Sr $5S^2\ {}^1S_o \rightarrow 5p\ {}^1P_1$ $\lambda = 4607.3$ Å
$5p\ {}^1P_1 \rightarrow 10s\ {}'S_o$ $\lambda = 4582.9$ Å
$5p\ {}^1P_1 \rightarrow 8d\ {}'D_2$ $\lambda = 4688.6$ Å

Absorption at 4607.3 Å was readily detected even at calculated vapor pressures of $5 \cdot 10^{-11}$ torr ($1.5 \cdot 10^6$ atoms/cc). At our highest temperature, 350°C, clear absorption was indeed observed at 4688.6 Å but none was ever found at 4582.9 Å. Thus the experiment demonstrates the possible applicability of IDLS to excited state spectroscopy in which the dye not only produces the excited state but also reveals its absorption spectrum to still higher levels.

4. Hydrogen Fluoride and Deuterium (ref. 4). The extremely high sensitivity of the IDLS technique was demonstrated by detection of HF in absorption in the third harmonic, $v=o\rightarrow 4$, using a 70 cm long intracavity cell containing 10 torr of HF. Individual rotational components were cleanly detected,

$P_4(1)$	6759.2 Å
$P_4(2)$	6780.8 Å
$P_4(3)$	6805.2 Å
$P_4(4)$	6832.5 Å

Then, to search for laser-induced chemistry, 22 torr of HF and 183 torr of D_2 were exposed to 10^4 dye laser flashes. Since the wavelengths correspond to 42 kcal/mole, the excitation energy should far exceed the activation energy for the exchange reaction,

$$HF^{\ddagger} + D_2 \rightarrow DF + HD$$

as judged by the activation energy of 13.8 kcal/mole for the corresponding HCl + D_2 reaction. Unfortunately, the D_2 contained 4.4% HD impurity before exposure to the dye laser. After exposure, the HD found was larger, 4.7%, but by an amount within experimental uncertainty.

5. $\underline{C_2H_4 + O_2}$ (ref. 4). Samples of 2 to 10 torr of C_2H_4 with and without a few percent O_2 impurity were flash photolyzed in a 38 cm suprasil coaxial flashlamp placed in the dye laser cavity. The IDLS dye laser probe was pulsed at various times during and up to 15 μsec after the flash. With no O_2 present, no absorptions were detected from 5750 to 6190 Å - thus C_2H_4 does not absorb in this region. In the presence of the O_2 impurity, absorption band heads at 6138 and 6144 Å were detected. The band heads correspond to known absorptions of HCO produced in chemical reactions of $C_2H_4^*$, O_2^*, and/or O atoms.

6. <u>Formaldehyde Photolysis</u> (ref. 4, 14). The photolysis of formaldehyde has recently been proposed as a candidate for laser-induced isotope separation[*]. The efficiency is strongly dependent on the branching ratio:

$$\begin{aligned} H_2CO + h\nu &\rightarrow H_2 + CO \\ &\rightarrow H + HCO \end{aligned}$$

Since HCO is readily detected in the IDLS technique, this system was carefully studied. Not only was HCO detected, but the rate constants of two important HCO reactions were measured:

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[*] P. L. Houston and C. B. Moore, J. Chem. Phys. 65, 757 (1976).

$$HCO + O_2 \rightarrow HO_2 + CO \qquad k = (4.0\pm.8)\cdot 10^{-12}\ cm^{-3}/\text{molecule sec.}$$

$$HCO + NO \rightarrow HNO + CO \qquad k = (1.45\pm.2)\cdot 10^{-11}\ cm^{-3}/\text{molecule sec.}$$

A variety of additional quantities were estimated, including the effect of photolysis wavelength on branching ratio, the rate of deactivation of vibrationally excited HCO, the carbonyl stretching frequency of electronically excited HCO, etc.

IV. Cryogenic Thermoluminescence (refs. 16,17).

When free radicals react in a cryogenic matrix (e.g., solid argon) electronically excited products have a significant opportunity to decompose radiatively because of apparently inefficient deactivation processes under these experimental conditions. Consequently, this type of experiment can provide a new avenue in the determination of the role of electronic degrees of freedom in chemical reactions. Obviously, any such technique will ultimately aid in the search for chemically pumped electronic lasers.

Some of the systems that have been studied successfully include the following systems:

$$N_2O + h\nu \rightarrow N_2 + O$$

$$O(^3P) + O(^3P) \rightarrow O_2^*(A\ ^3\Sigma_u^+)$$

$$O_2^*(A\ ^3\Sigma_u^+) \rightarrow O_2(X\ ^3\Sigma_g^-) \quad \text{(Herzberg bands)}$$

The Herzberg bands are observed when solid $N_2O/Ar = 1/100$ mixtures are photolyzed for an hour at 8°K and then warmed to 10-14°K. The observed progression is shifted to higher frequencies by 209 cm^{-1} and the vibrational spacing is raised about 13 cm^{-1} relative to the gas phase.

$OCS + h\nu \rightarrow CO + S$

$S(^3P) + S(^3P) \rightarrow S_2^*$

$S_2(B\ ^3\Sigma_u^-) \rightarrow S_2(X\ ^3\Sigma_g^-)$ (Schumann-Runge-equivalent)

$S_2(c\ '\Sigma_u^-) \rightarrow S_2(a\ '\Delta_g)$

$S_2(A'\ ^3\Delta_u) \rightarrow S_2(X\ ^3\Sigma_g^-)$

The photolysis of OCS in solid Ar, Kr, Xe, and SF_6 has been studied. In every case, warming a few degrees induces thermoluminescence readily attributed to diffusion and reaction of ground state sulfur atoms. The highest frequency progression, in the range 3300 to 5200 Å, closely resembles the fluorescence-induced S_2 B→X transition, the equivalent to the O_2 Schumann-Runge bands. In addition, there are two additional, distinct progressions at longer wavelengths, neither detected before by any spectroscopic technique. The vibrational intervals indicate that the longer wavelength transition in the spectral region 6700-8800 Å must terminate in the ground state, $X\ ^3\Sigma_g^-$. A variety of data indicate that the progression can be assigned to the S_2 A'→X transition. Between these two progressions lies another, weaker progression whose vibrational intervals indicate that the ground state of S_2 is not involved. Once again, a variety of arguments lead to a rather definite assignment to the S_2 c→a transition.

The observation of electronic transitions never before detected for a molecule as well known as S_2 suggests that this thermoluminescence technique will be of particular interest. As further support of this optimistic view, we already have detected cryogenic thermoluminescence from SO_2, SO, and two or three other reaction products whose identity is not yet positive. We believe that this novel technique will be an aid in our understanding of chemical pumping of electronic degrees of freedom.

Personnel

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3.	Ole D. Krogh, Graduate Student, Postdoctoral	Assistant Professor, Univ. of Auburn, Auburn, Alabama
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5.	Eric Sirkin, Graduate Student	(continuing)
6.	Yuan-Pern Lee, Graduate Student	(continuing)
7.	Geri Richmond, Graduate Student	(continuing)
8.	Donald K. Stone, Computer Programmer	(continuing)
9.	Dolly Martin, Secretary	(continuing)

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2. E. Cuellar-Ferreira, Ph.D. Dissertation, University of California, Berkeley (1975): "Chemical Lasers Based Upon Rotational Transitions."
3. O. D. Krogh, Ph.D. Dissertation, University of California, Berkeley (1976): "Mechanisms and Energy Distributions for the Reactions between Hydrogen and Chlorine Fluorides through Chemical Laser Studies."
4. J. P. Reilly, Ph.D. Dissertation, University of California, Berkeley (1977): "Probing Optical Transitions with Intracavity Dye Laser Spectroscopy."

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16. "Thermoluminescence of S_2 in Cryogenic Samples", Y. P. Lee and G. C. Pimentel (in preparation).

17. "Thermoluminescence of SO in Cryogenic Samples", Y. P. Lee and G. C. Pimentel (in preparation).

18. "ClF_x-H_2 Chemical Lasers: Vibration-Rotation Emission by HCl", O. D. Krogh and G. C. Pimentel (in preparation).

19. "HF Rotational Laser Emission by the ClF-H_2 Chemical Laser", E. Cuellar and G. C. Pimentel (in preparation).