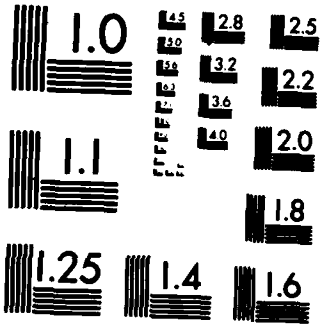
AD-A147 431 LASER SPECTROSCOPY OF ALKALI ATOM-TETRAHALOETHYLENE REACTIONS(U) NEW HAMPSHIRE UNIV DURHAM DEPT OF PHYSICS J W WRIGHT AUG 84 AFWL-TR-83-132 F29601-82-K-0068 1/1

UNCLASSIFIED F/G 7/2 NL

END


1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

(2)

AFWL-TR-83-132

AFWL-TR-
83-132

LASER SPECTROSCOPY OF ALKALI ATOM-TETRAHALOETHYLENE REACTIONS

John J. Wright

University of New Hampshire
Department of Physics
Durham NH 03824

August 1984

Final Report

Approved for public release; distribution unlimited.

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117

AFWL-TR-83-132

This final report was prepared by the University of New Hampshire, Durham, New Hampshire, under Contract F29601-82-K-0068, Job Order ILIR8224 with the Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico. Steven J. Davis (ARDD) was the Laboratory Project Officer-in-Charge.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

If your address has changed, if you wish to be removed from our mailing list, or if your organization no longer employs the addressee, please notify AFWL/ARDD, Kirtland AFB, NM 87117 to help us maintain a current mailing list.

This technical report has been reviewed and is approved for publication.

Steven J Davis
STEVEN J. DAVIS
Project Officer

FOR THE COMMANDER

Orven F. Swenson	Winston K Pendleton
ORVEN F. SWENSON	WINSTON K. PENDLETON
Maj, USAF	Col, USAF
Chief, Short Wavelength Laser Branch	Chief, Director Energy Technology Off

---

DO NOT RETURN COPIES OF THIS REPORT UNLESS CONTRACTUAL OBLIGATIONS OR NOTICE ON A SPECIFIC DOCUMENT REQUIRES THAT IT BE RETURNED.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFWL-TR-83-132

6a. NAME OF PERFORMING ORGANIZATION
University of New Hampshire
Department of Physics

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Air Force Weapons Laboratory

6c. ADDRESS *(City, State and ZIP Code)*
Durham NH 03824

7b. ADDRESS *(City, State and ZIP Code)*
Kirtland Air Force Base NM 87117

8a. NAME OF FUNDING/SPONSORING ORGANIZATION

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F29601-82-K-0068

8c. ADDRESS *(City, State and ZIP Code)*

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61101F	ILIR	82	24

11. TITLE *(Include Security Classification)* LASER SPECTROSCOPY OF ALKALI ATOM-TETRAHALOETHYLENE REACTIONS

12. PERSONAL AUTHOR(S)
Wright, John J.

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM 82 Jun TO 83 Dec

14. DATE OF REPORT *(Yr., Mo., Day)*
1984, August

15. PAGE COUNT
22

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Laser, Alkali Atoms, Chemiluminescence, Spectroscopy, Sulfur, Carbon, Hydrocarbons, Mass Spectroscopy

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

The results of a series of experiments are reported to determine the origin of the chemiluminescent spectrum observed in reactions of alkali metal atoms with vapors of C_2Cl_4 and similar halogenated C_2 molecules. The emission was observed to be independent of the alkali atom and the halogen atom and, hence, attributed to a previously unobserved state of a carbon molecule, such as C_2, C_3, or C_4. Null results from laser spectroscopy suggest the emission is not to the ground state of the molecule. Initial gain measurements were also negative. These reactions are being investigated using mass spectroscopy with the aim of determining the source of the chemiluminescence and the molecular dynamics of this and related reactions.

During the course of this research, several other chemiluminescent reactions were discovered which are also promising candidates for future investigation. The primary result from this research is that the stripping of halogen atoms from parent molecules by alkali atoms (Over)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Steven J. Davis

22b. TELEPHONE NUMBER *(Include Area Code)*
(505) 844-1871

22c. OFFICE SYMBOL
ARDD

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

19. ABSTRACT (Continued)

is an exothermic process capable of producing electronically excited atoms and molecules and has apparently received little attention in the past.

I. INTRODUCTION

The potential for an electronic transition chemical laser from C_2 Swan band chemiluminescence produced in the reactions of alkali atoms with CCl_4 vapor has generated worldwide interest. Palmer and Miller (Ref. 1) first reported chemiluminescence from alkali-carbontetrahalide reactions followed by similar observations from a Russian group headed by Bugrim, et al (Ref. 2). Subsequently, Miller and Palmer (Ref. 3) and Naegeli and Palmer (Ref. 4) showed that the populations of the vibrational levels of the excited C_2 state were inverted. More recently, a Chinese group, Xuechu and Nanquan (Ref. 5) and Wang et al (Ref. 6), and Luria et al (Ref. 7) have studied the relaxation kinetics of the excited C_2 during the reaction. The dynamics of the reaction are still unknown except that the spectrum must result from a recombination of carbon atoms and/or molecules.

This report describes the preliminary results of similar types of reactions with alkali atoms and tetrahaloethylene molecules, such as C_2Cl_4, which produce a very different and anomalous blue-green chemiluminescence (Ref. 8).

II. EXPERIMENTS

Figure 1 is a schematic diagram of the experimental arrangement used for most of the experiments which will be discussed in this report. The reactions took place in a 300 ml evacuated Pyrex cell attached to a vacuum-gas handling system. The cell contained an alkali metal and was heated to maintain alkali vapor pressures in the range 1 - 100 Pa. The C_2Cl_4 was admitted to the cell through a controlled leak at a rate necessary to establish a uniform luminescent glow throughout the cell. The chemiluminescent spectra were recorded with an optical multichannel analyzer.

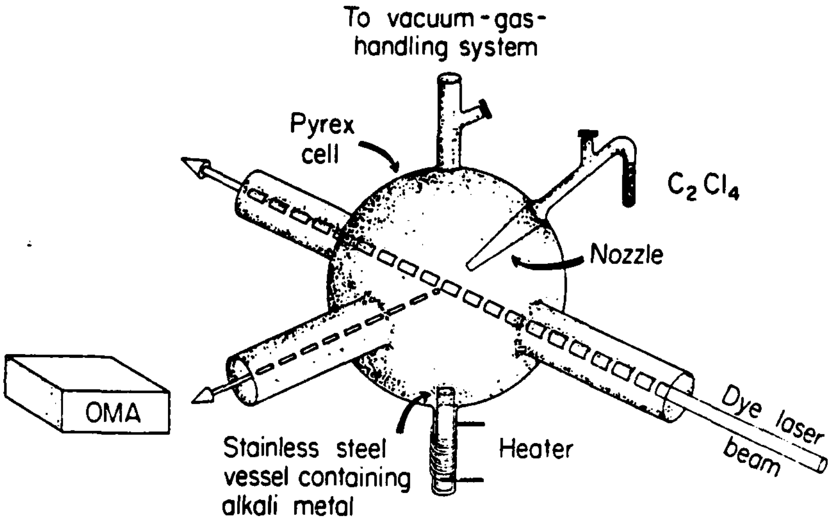


Figure 1. Experimental arrangement.

1. BLUE-GREEN SPECTRUM

The blue-green spectrum was observed in the following reactions: Li,Na,K,Rb,Cs + C_2F_4, Na,K,Rb,Cs + C_2Cl_4, Na,K,Rb,Cs + $CF_3(CF_2)_4CF_3$ (perfluorohexane), Na,K,Rb,Cs + $CF_3(CF_2)_4CF{=}CF_2$ (perfluoroheptene), Cs + $CCl_2F\text{-}CClF_2$ (trichlorotrifluoroethane), K,Rb + $CF_3CF_2CF_2I$ (perfluoropropyl iodide), and Cs + C_4F_8. Figure 2 shows some representative spectra. The spectra are independent of the alkali atom involved and the halogen atom.

The common element is the presence of more than one carbon molecule.

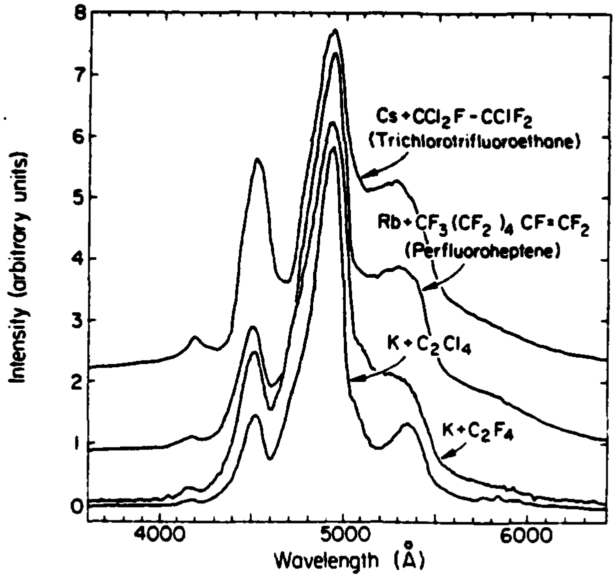


Figure 2. Representative blue-green spectra.

The spectral source has been narrowed further because it was discovered that the molecule must have carbon atoms bonded to carbon atoms, i.e. there must be either a C-C or C=C bond in the reactant molecule. The reaction with $Cl_3COCOCl$ produces an inverted Swan spectrum of C_2 identical to that from the reaction of CCl_4 (Fig. 3). In this molecule, the carbon atoms are not bonded to each other but to a common oxygen atom.

There is also evidence that the reaction producing the blue-green spectrum requires at least one stripped C_2 molecule. The reaction with trichloroethylene (C_2HCl_3) did not produce either the blue-green spectrum or the C_2 Swan spectrum. The alkali halogen bond energy is greater than the carbon-halogen bond energy so the alkalis can strip halogens away from the carbon but the alkali-hydrogen bond energy is less than the carbon-hydrogen bond energy so in this reaction the stripping by the alkalis results in C_2H molecules.

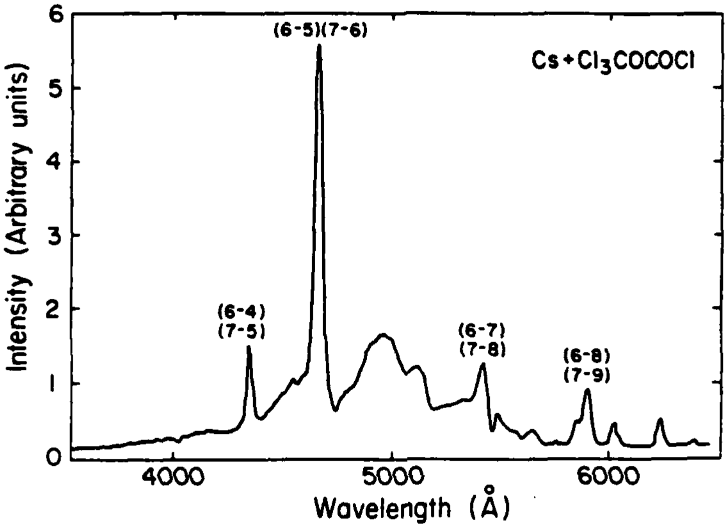


Figure 3. Population inverted C_2 Swan spectrum.

In the reaction K + CCl_4, it was reported in Reference 4 that the population inversion in the Swan spectrum of C_2 was independent of Argon (Ar) buffer gas pressure from 25 to 2500 Pa. Luria (Ref. 7) measured a quenching rate for the excited state of C_2 due to Ar and Xueche (Ref. 5) has subsequently confirmed this (for Na + CCl_4) and found the quenching rate to be nearly gas kinetic. The reactions of alkalis with CCl_4 observed in this laboratory showed no vibrational relaxation with 2.6×10^4 Pa of He or 1.3×10^4 Pa of N_2 buffer gas. Similar results with C_2Cl_4 and the blue-green spectrum. Figure 4 shows the results of adding 25 torr (3325 Pa) of He to a Cs + C_2Cl_4 reaction cell. The blue-green spectrum is unaltered. The addition of two atmospheres of He did not alter the spectrum other than to reduce the intensity due to the reduced diffusion rate.

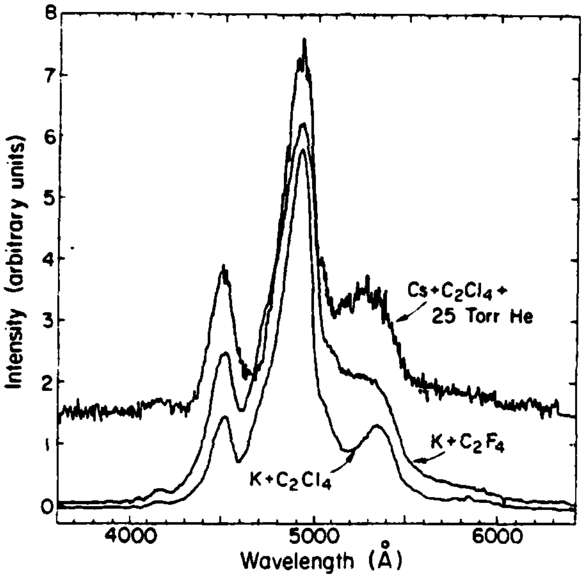


Figure 4. Effect of buffer gas on the blue-green spectrum.

In its high resolution mode, the OMA has a resolution of 1.4 angstroms per channel. With this resolution, the blue-green spectrum still appears structureless.

2. LASER SPECTROSCOPY

Numerous laser spectroscopy experiments using continuous wave and pulsed dye lasers and an Ar^+ laser failed to produce any detectable laser induced emission from reaction cells. The Ar^+

laser has several lines which overlap the observed blue-green emission. No laser induced fluorescence was detected during the reaction due to absorption of Ar^+ laser light. In an attempt to monitor the observed blue-green emission as a function of C_2 density (and to determine if C_2 was present) the cw dye laser was tuned to the 1-0 transition (5635 A) of the C_2 Swan system and the N_2-pumped dye laser was tuned to the 0-0 transition (5165 A) of the same system and passed through reaction cells burning Cs and K + C_2Cl_4 and perfluorohexane. No C_2 emission was ever observed. However, this is not conclusive evidence that C_2 is not present since laser induced emission was not detected in a DC discharge in C_2Cl_4 which produced C_2 Swan band emission. The lower state of the Swan system is not the ground X state of C_2 but lies about 700 cm^{-1} above it. The near infrared X - A transitions of C_2 could not be directly excited but A - X emission was never observed from either the alkali-CCl_4 or alkali-C_2Cl_4 reactions.

3. GAIN MEASUREMENTS

Several attempts were made to detect gain from the blue-green emission using the 4880 Ar^+ laser line and a multiple-pass reaction cell as shown schematically in Figure 5. Each laser pass went through about 10 cm of the reaction volume. The following configurations were attempted: 9 passes through Rb + perfluoroheptene, 9 passes through Cs + perfluorohexane, 7 passes through K + perfluorohexane and 5 passes through the same reaction with the laser beam expanded to fill the volume, and Cs +

perfluorohexane with a buffer gas added. The results were all negative. Future gain measurements are planned monitoring the decay time of the N_2-pumped dye laser pulse and a reaction cell inside an etalon cavity. This arrangement will circumvent the problems encountered in these experiments with laser beam jitter and refraction effects.

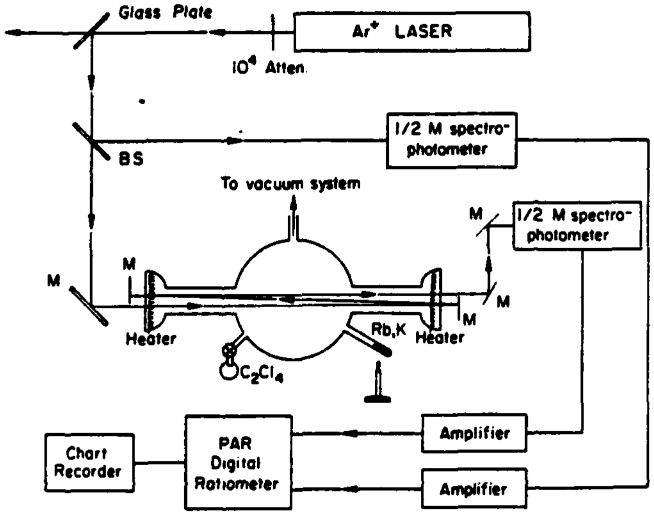


Figure 5. Gain measurement apparatus.

4. MASS SPECTROSCOPY

Since laser spectroscopy was unable to shed any light on the origin of the blue-green emission, it was decided to try mass spectroscopy. The aim was, and still is, to monitor the reaction products as a function of the reactant densities and blue-green emission to determine the source of the emission and the reaction dynamics. The Air Force Weapons Laboratory loaned a mass spectrometer for this purpose. It was determined that the reaction could be run into the spectrometer and that reaction products could be detected during and after the reaction. The cracking by the mass spectrometer makes it difficult to distinguish reaction products from mass spectrometer cracking products. Several runs were made with inconsistant results before it was realized that reactions with the alkali metal on the cell walls was the dominate effect that was observed with the mass spectrometer. A new cell configuration was designed, but before it could be tested, the mass spectrometer self-destructed. Subsequently, a quadrupole gas analyzer was purchased and the work is continuing.

5. OTHER RELATED EXPERIMENTS

During the course of these experiments several other interesting effects were observed which will be investigated further. To summarize the basic findings, the gas phase reaction of alkali metal atoms with halogenated molecules is exothermic and produces excited states in a variety of atoms and molecules.

a. C_3 Spectrum Figure 6 shows the spectrum obtained from the reaction of Cs and C_3F_7I (perfluoropropyl iodide). In addition to the usual blue-green spectrum and some atomic Cs lines, there is the Comet Tail spectrum of C_3 which peaks around 4050 A. To our knowledge, this is the first observation of a chemically produced C_3 spectrum.

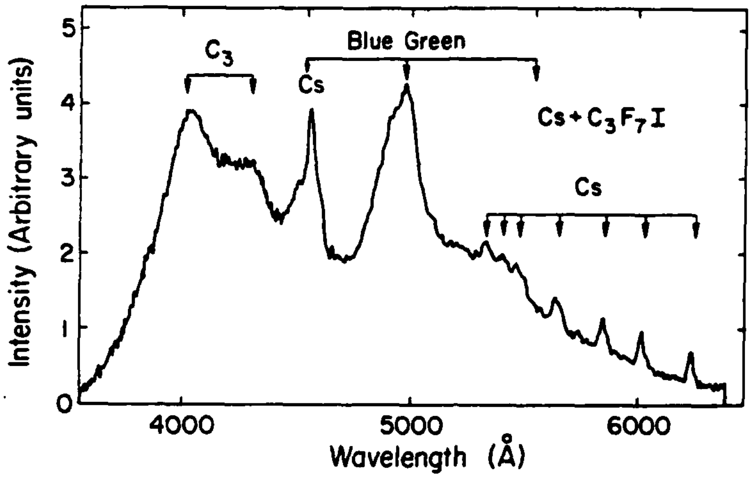


Figure 6. Chemically produced C_3 spectrum.

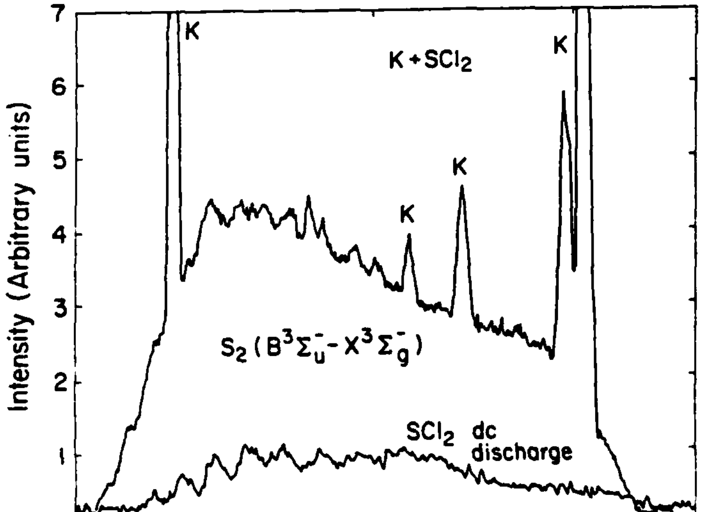


Figure 7. Chemically produced S_2 spectrum.

b. S_2 Spectrum Figure 7 shows a typical spectrum from the reaction of K and SCl_2. Analogous to the reaction with CCl_4 producing the C_2 recombination Swan spectrum, the reaction with SCl_2 produces electronically excited S_2. The emission has been identified as that from the B - X system, which is a known lasing system.

c. Atomic Cs Spectrum The reaction of Cs atoms with SCl_2 does not produce the recombination spectrum of S_2 shown in Figure 7 but produces a bright flame which consists almost entirely of atomic Cs lines. Figure 8 shows part of the spectrum. The transitions identified originate from the s and d states of the n=7, 8,9,10,11, and 12 levels and terminate at the 6p state. There are several infrared transitions which are allowed but which are outside the range of the detector. These high lying Rydberg states have progressively longer lifetimes and it is possible that population inversions exist between some of these upper levels.

d. K_2 Spectrum In the process of trying to understand the dynamics of the C_2 Swan system production, an attempt was made to alter the vibrational populations with inert buffer gases. As stated earlier, there was no buffer gas effect with the K + CCl_4 reaction. However, Figure 9 shows that the addition of a buffer gas to the reaction of K + CBr_4 produced a more thermal vibrational distribution in the Swan spectrum of C_2. (This new information was considered to be relatively useless since it could not be determined whether the effect of the buffer gas occurred before or after the formation of C_2 molecules.) Figure

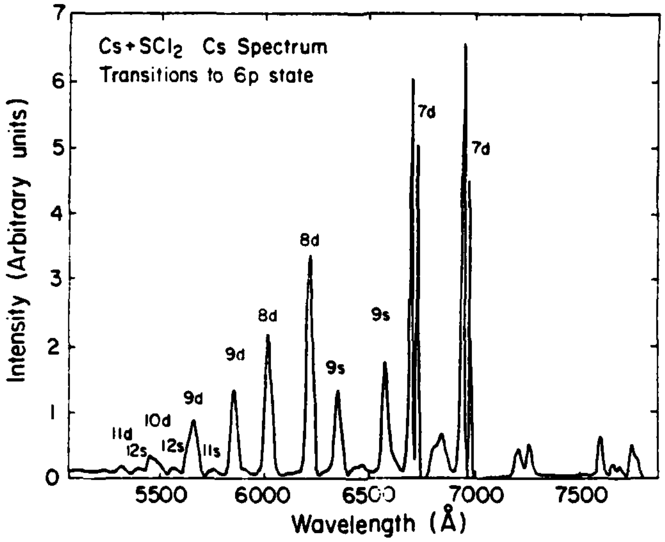


Figure 8. Chemically produced Cs Rydberg series.

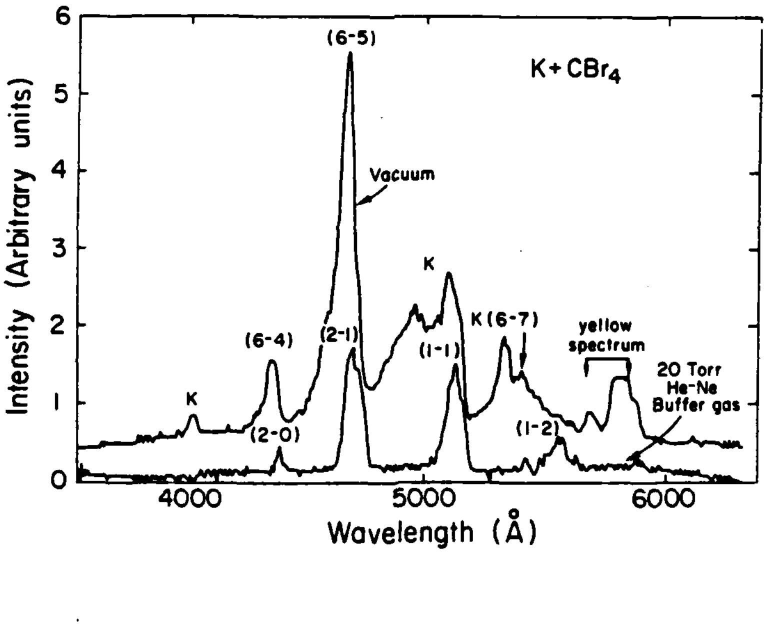


Figure 9. Vibrational relaxation of the C_2 Swan system.

9 also shows a yellow emission in the range 5700-5850A. Under the proper conditions, this spectrum dominated the flame, at which time the entire cell glowed yellow and the OMA showed no other spectral components. The effect was reproducible. Figure 10 shows this yellow spectrum under higher resolution. It has not been identified but the most likely candidate, on the basis of elimination, is K_2. The Rb + CBr_4 reaction showed no such spectrum and neither did the reaction of K + Br_2 or CI_4. This effect will be investigated further.

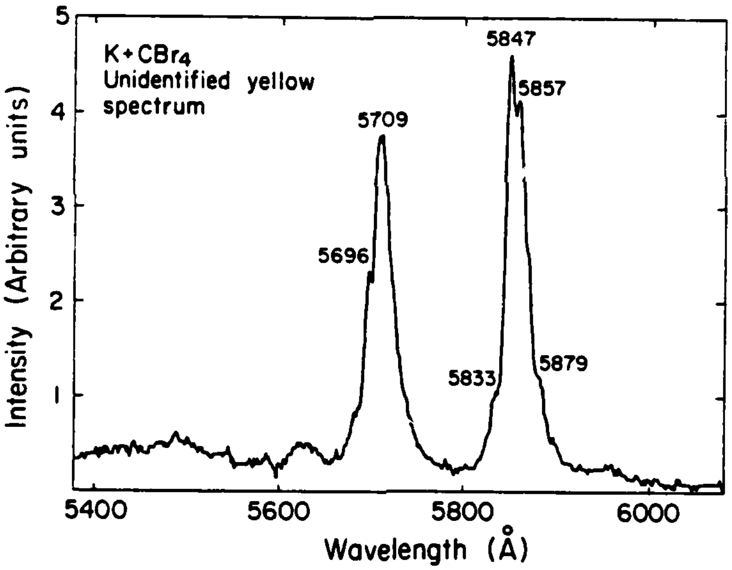


Figure 10. Unidentified yellow spectrum from K + CBr_4.

III. CONCLUSIONS

An extensive amount of spectroscopic information has been accumulated on the chemiluminescent reactions of alkali atoms with halogenated hydrocarbons but as yet the source of the anomalous blue-green luminescence has not been identified. The observation of this anomalous emission was reported in a previously published paper (Ref. 8) and it was speculated that the source might be C_4 molecules. This was based on theoretical calculations of the C_4 spectrum and an analogy between CCl_4 producing C_2 emission and C_2Cl_4 producing C_4 emission. This explanation cannot be ruled out. Other possibilities include previously unobserved C_2 emission from high lying levels of the A state (i.e. A - X emission) or highly perturbed Swan emission. Apparently, little is known about the structure of the A state for v' greater than 8 because these levels are not easily accessible from the lower levels of the X state and recombination (observed in discharges) favors formation of the triplet system, i.e., Swan band emission. If it is dimer emission, it is difficult to account for the broad, unstructured emission width and why C_2 Swan emission is not observed. Another possibility is emission form an intermediate process. In C_2Cl_4 the carbon atoms share a double bond. In C_2Cl_2 the carbon atoms share a triple bond. The difference in bond energies is about 58 kcal/mole or 5000 A. It may be possible that when an alkali strips a Cl atom from double bonded C_2Cl_3 to produce triple bonded C_2Cl_2 the energy is given up radiatively. This might be independent of the alkali and halogen and account for the broad emission width. The four emission peaks may reflect the order in which the halogen atoms are stripped. Yet another possibility is previously unobserved emission from C_3 molecules. It is hoped that the new mass spectrometer will provide the additional information necessary to determine the source of this emission.

Since there is considerable interest in the dynamics of the alkali-CCl_4 reaction, it is hoped that the use of the mass spectrometer will shed light on this system as well. The analysis in this case is simplified because the emission is known to originate from C_2 molecules.

The main conclusion drawn from this research is that the reactions of alkali atoms with halogenated molecules produce excited states of molecules and atoms, several of which are previously unobserved. Continued research on the molecular dynamics involved in these reactions should enhance the basic knowledge and aid the search for an electronic transition chemical laser.

REFERENCES

1. H.B. Palmer and W.J. Miller, "Energy Distribution in Products of the Reaction of C atoms with CH and CCl," J. Chem. Phys., **38**, 278 (1963)

2. D.E. Bugrim, A.I. Lyutyi, V.S. Rossikhin, and I.L. Tsikora, "Excitation Characteristics of the Swann Bands of C_2 in Streams of Vapors of Metals and Organic Compounds," Optics Spectrosc., **19**, 320 (1965)

3. W.J. Miller and H.B. Palmer, "Chemiluminescence and Radical Reactions in Diffusion Flames of Alkali Metals with Organic Halides," J. Chem. Phys., **40**, 3701 (1964)

4. D.W. Naegeli and H.B. Palmer, "Creation of Population Inversion in the Triplet State of C_2 by Chemical Reaction," J. Chem. Phys., **48**, 2372 (1968)

5. Li Xuechu and Lou Nanquan, "The Vibrational Polulation Inversion and Relaxation Kinetics of the C_2 Triplet State," Chem. Phys. Letters, **75**, 110 (1980)

6. Wang Xiuyon, Li Xuechi, and Lou Nanquan, "Chemiluminescent Spectra of C_2 (d-a) and Deactivation of the C_2 d State in Na Vapor," Chem. Phys., **61**, 25 (1981)

7. M. Luria, D.J. Eckstrom and S.W. Benson, "Heat-Pipe-Oven Reactor (HPOR): I. A New Device for Flame Studies; Photon Yields in the Reaction of Na with CCl_4 and N_2O," J. Chem. Phys., **64**, 3103 (1976)

8. L.C. Balling and J.J. Wright, "Anomalous Chemiluminescence in Reactions of Alkali Atoms with C_2Cl_4 and C_2F_4," Chem. Phys. Letters **87**, 139 (1982)