

RADC-TR-71-293  
Technical Report  
June 1971



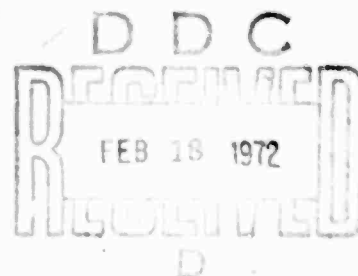
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**A SPECTRUM OF NEW EXPERIMENTS TO INVESTIGATE  
ALKALI METAL CHEMISTRY IN THE E REGION**

**Lockheed Missile & Space Company  
Palo Alto Research Laboratory**

**Sponsored by  
Advanced Research Projects Agency  
ARPA Order No. 1649**

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UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

## 1. ORIGINATING ACTIVITY (Corporate author)

Lockheed Missiles & Space Co  
3251 Hanover Street  
Palo Alto, CA

## 2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

## 2b. GROUP

## 3. REPORT TITLE

A Spectrum of New Experiments to Investigate Alkali Metal Chemistry  
in the E Region

## 4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report - Interim

## 5. AUTHOR(S) (First name, middle initial, last name)

J.B. Kumer

## 6. REPORT DATE

June 1971

## 7a. TOTAL NO. OF PAGES

23 30

## 7b. NO. OF REFS

28

## 8a. CONTRACT OR GRANT NO.

F30602-71-C-0029

a. PROJECT NO. ARPA Order 1649

-Program Code OE20

## 9a. ORIGINATOR'S REPORT NUMBER(S)

## 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

RADC-TR-71-293

## 10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

## 11. SUPPLEMENTARY NOTES Monitored by

VINCENT J. COYNE  
RADC/OCSE  
Griffiss AFB NY 13440

## 12. SPONSORING MILITARY ACTIVITY

Advanced Research Projects Agency  
1400 Wilson Blvd  
Arlington VA 22209

## 13. ABSTRACT

This report discusses in general the chemistry of alkali metals in the upper atmosphere and the relationship between the E Region metal chemistry and alkali metal chemistry. A discussion on the merit of performing various experiments to investigate E Region metal (alkali metals and metal ions) chemistry is presented.

**UNCLASSIFIED**

Security Classification

14.

KEY WORDS

LINK A

LINK B

LINK C

ROLE

WT

ROLE

WT

ROLE

WT

Alkali Metal Chemistry

E Region

Metal Oxides

**UNCLASSIFIED**

Security Classification

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**J. B. Kumer**

**Contractor: Lockheed Missile & Space Company  
Palo Alto Research Laboratory  
Contract Number: F30602-71-C-0029  
Effective Date of Contract: 1 May 1970  
Contract Expiration Date: 31 April 1971  
Amount of Contract: \$98,300.00  
Program Code Number: OE20**

**Principal Investigator: Dr. Billy M. McCormac  
Phone: 415 324-3311-Ext 45315**

**Project Engineer: Vincent J. Coyne  
Phone: 315 330-3107**

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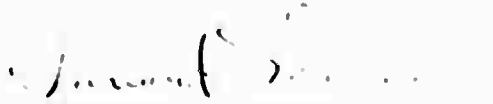
**This research was supported by the  
Advanced Research Projects Agency  
of the Department of Defense and  
was monitored by Vincent J. Coyne,  
SADC (OCSE), GAFB, NY 13440 under  
Contract F30602-71-C-0029**

## FOREWORD

This report was prepared at Lockheed Palo Alto Research Laboratory, Palo Alto, California 94304, for the Advanced Research Projects Agency, Washington, D.C. Rome Air Development Center, Griffiss Air Force Base, New York, is monitoring the study for ARPA, under CONTRACT Number F30602-71-C-0029, Project 1649. Mr. Vincent J. Coyne (OCSF) is the RADC Project Engineer.

## PUBLICATION REVIEW

This technical report has been reviewed and is approved.

  
VINCENT J. COYNE  
RADC Project Engineer

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## Section 1

### INTRODUCTION

An understanding of the chemistry of metals deposited in the mesosphere by nuclear blasts is essential to our country's defense. A significant step in this direction would be to establish an understanding of the chemistry of the naturally occurring metals in the E-region. The metals of primary interest are Li, Fe, and Al. The chemistry of the naturally occurring metals is poorly understood at present. A wide range of new experiments that could elucidate the chemistry of the alkali metals (Li, Na, K and  $\text{Ca}^+$  and  $\text{Mg}^+$  ions which have alkali metal electronic structure) are discussed in this paper.

This paper is structured as follows. There are five sections including the Introduction. A brief review of the problem of alkali metals in the upper atmosphere is given in Section 2. The E-region metal ion problem and its relation to the alkali metal problem is discussed in Section 3. A number of valuable new experiments aimed towards elucidating the E-region metal problem (alkali metals and metal ions) are described in Section 4. The experiments are summarily listed and classified as to technological and economic feasibility in Section 5.

## Section 2

### THE ALKALI PROBLEM

The alkali metal problem with special emphasis on Na is thoroughly reviewed by Hunten, 1967. It is also discussed more briefly in several recent reviews (Rundle, 1971; Llewellyn and Evans, 1971; Hunten, 1971). This section contains a further review with emphasis on the most recent experimental developments.

#### 2.1 Alkali Metal Observations

Rundle (1971) lists five significant features of the Na column density variations. Not all of these variations have been confirmed for the other alkalis. Confirmations will be noted. The variations are as follows.

2.1.1 There is a seasonal variation exhibiting maximum column densities (or abundance) in the winter. The amplitude of this variation increases with higher latitudes. This variation is present for Li.

There is also a seasonal variation in the differences between the altitudes of consecutive morning and evening twilight layers. This effect has also been observed for Li (Sullivan, 1970).

2.1.2 There are temporal variations with periods of about a month during winter and at high latitudes. These have been associated with stratospheric warmings (Hunten and Godson, 1967).

2.1.3 Diurnal variations with the Na abundance 2 to 4 times greater at local noon than at either morning or evening twilight have been reported. No detectable differences between morning and evening twilight abundances have been observed. Laser studies (Sandford and Gibson, 1970) have shown that Na abundances remain essentially constant during the night. The diurnal variation has not been conclusively demonstrated for K (Albano et al., 1970).

2.1.4 The layer always peaks in the 90-95 km region. This is true for all the alkalis. Nighttime laser studies essentially confirm this for Na while uncovering some new and stimulating aspects of the problem.

2.1.5 Small topside scale heights of 2-4 km are recorded in all measurements. Bottomside scale heights are also quite steep and the layer peaks somewhat higher than one might expect from the simple chemical theory described in Section 2.2.1.

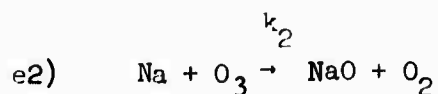
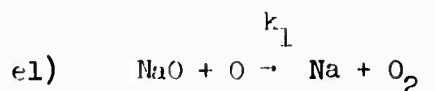
2.1.6 The credibility of the noon increase in the daytime Na abundance has recently come into question (Albano et al. 1970; Llewellyn and Evans, 1971). The diurnal variation of the Na abundance has primarily been observed by daytime Zeeman photometry. Standard techniques in daytime Zeeman photometry are vulnerable to contamination via the Ring Effect. This effect has been reported and discussed in the literature (Grainger and Ring, 1962; Hunten, 1970). Here it suffices to say that if one uses standard techniques of daytime Zeeman photometry one is not able to quantitatively say how much of the observed noon increase in Na abundance is real and how much is an artifact of the Ring Effect. Albano et al. state that it is possible in principle to operate Zeeman photometers in the daytime in such a way that the results are free of Ring Effect contamination. At present they are developing such a technique. They are also investigating the extent of the contamination of results that have been obtained using standard techniques.

## 2.2 Models of the Na Layer

Rocket experiments detecting the steep topside scale heights of the Na layer led investigators to abandon the purely chemical theory of its production and maintenance. Recent observations of the nighttime layer via laser radar will also force investigators to seriously reconsider the current models of the Na layer. This is due to the observed persistence of the steep topside scale height throughout the night.

2.2.1 Since the modern models still must deal with chemistry a brief review of the purely chemical model is given below.

Four reactants are involved in the simplest of these models. They are NaO, Na, O, and O<sub>3</sub>. Production of Na occurs via



Equating loss to production gives the ratio of Na to NaO as

$$e3) \quad \frac{(\text{Na})}{(\text{NaO})} = \frac{k_1}{k_2} \frac{(\text{O})}{(\text{O}_3)} = 7 \frac{(\text{O})}{(\text{O}_3)}$$

According to this model a transition region exists where  $(\text{O})/(\text{O}_3) = 1/7$ . Slightly below this region all the sodium is in the form NaO and slightly above it is all Na.

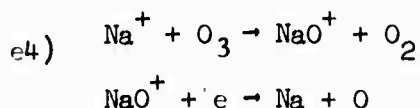
This model predicts a topside scale height for Na that is equal to that of the ambient atmosphere. Observed scale heights are 2-4 km compared with atmospheric scale heights of 6 km forcing one to more complicated models.

2.2.2 Donahue's (1967) model invokes a  $V \times B$  wind shear concentrated layer of negatively charged dust particles as the source of Na atoms. The dust layer is very narrow, less than 1 km thick. This narrow source of Na atoms naturally explains the steep top and bottom scale heights of the Na layer via the diffusive flow of Na to adequate removal mechanisms located both below and above the source. The lower removal mechanism is provided by reaction e2). The lack of an obvious removal mechanism above the source is a weak point of this model. Note that if the source of Na is assumed to be a  $V \times B$  windshear concentration of negatively charged dust particles then it is impossible to remove the Na above the source by ionization to  $\text{Na}^+$  followed by a wind induced  $V \times B$  force that sweeps the positive ions down to a molecular sink below the source as is postulated in Gadsden's model (see Section 2.2.4 below).

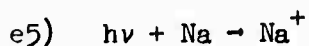
2.2.3 Hunten (1967) invokes a dust bank model with the dust settling out so that it has a much steeper scale height (above  $\sim 90$  km) than that of the atmosphere. The dust acts as a source and sink of free Na. During the day the sun "boils" free Na off the dust and at night the Na condenses

on the dust particles. This model predicts shallow topside scale heights during the nighttime and hence must be rejected. The dust bank hypothesis may however serve as a springboard for new attempts at model building (Rundle, 1971).

2.2.4 Gadsden invokes a narrow source of atomic Na followed by upwards diffusion (explaining the steep scale height) followed by ionization to  $\text{Na}^+$  followed by a wind induced  $\mathbf{V} \times \mathbf{B}$  force that sweeps the ions down to a molecular sink somewhere below 90 km. Hanson and Donaldson (1967) use essentially the same model except they do not sweep their  $\text{Na}^+$  ions to a molecular sink but instead rejuvenate them as free Na that may diffuse upwards again via the reaction



Both of these models, as stated, are in trouble at night when the supposed source of ionization



is shut off.

## 2.3 Research Priorities Established at the Aurora and Airglow 1970 Conference

It was suggested that more and better observations are necessary. Some experiments currently in progress and working towards this end are briefly discussed in Section 4.1. Llewellyn and Evans (1971) pointed out that a proper evaluation of the Ring Effect may lead to significant modification in the results of Zeeman photometry concerning the diurnal variation. Albano, et al. are currently working on this. Rundle suggested that we could do a better job in our theoretical modeling.

B. McCormac (1970) pointed out that a measurement of the total Na inventory (or that of any E-region metal) would be very valuable. Some means of achieving this end are examined in Section 4.2.

Section 3  
E-REGION METAL ION LAYERS  
THEIR RELATION TO THE ALKALI METALS

3.1 Metal Ion Observations

Narcisi (1968) and Young and Holmes (1967) have reported interesting results concerning metal ions in the E-region. Typically they find a narrow layer of metal ions peaking at 90-95 km just as the neutral alkali metals do. The layer is similar in structure to that of the alkali layers. The composition of the metal ion layers strongly suggests a meteor origin. (See Table I, Column F.) The abundance of all the metal ions under quiet conditions is roughly equal to that of the neutral Na layer. The ratio  $(Na^+)/Na \sim 1/10$  (with much uncertainty). Neutral metal atoms certainly accompany the metal ion layer. Some of the metal monoxides and dioxides may also be present.

3.2 The Relation to the Alkali Metal Problem

In view of this data it is likely that a successful model of the Na layer might as a by product explain the metal ion problem and vice versa. Narcisi (1968) has made a beginning in this direction. The strongest link between the two problems is the question of the origin of metals in the upper atmosphere. The common link in the chemistry is their subsequent removal. Standard Na layering models, described in Section 2.2 above, typically invoke some kind of aerosol source. The end products of metal removal are usually assumed to be molecular compounds. Metal oxides, hydrides, hydroxides, nitrates, carbonyls and carbonates are some of the candidates for these compounds. In order to precisely determine the relative abundances of metals in the source aerosol one must as a first step measure the total inventory of several metallic species, that is, the sum of the neutral atoms, the ions and the molecular compounds of a given metal for several different metal species. The measurement of the altitude profiles of the concentrations of the various chemical forms of a given metal would provide information directly related to that metal's chemistry.

Table I

Column densities of metal atoms and ions found in measurements and estimates of those needed for twilight and laser measurements†

Column Densities (x 10 <sup>3</sup> cm <sup>-2</sup> )									
Metal Radiation or Ion Feature	Oscillator Strengths	Relative Abundances		* g photons sec·molecule	** Typical Measurements	Upper Limits (Gadsden, 1969)	Minimum Detectable via Twilight Photometry	Minimum Detectable by Laser	
		Meteor	Sea Water						
Na 5890	.65	.027	1.0	.54	25,(1-4)		.093	1.0	
Li 6708	.40		6 x 10 <sup>-7</sup>	8.7	.025	.16	.0057	1.22	
K 7699	.33	.0023	.095	1.92	.125	14.10	.026	2.0	
Sr 4607	2.09		.017	.81		.28	.062		
Cr 4254	.081	.005		.037		6.5	1.35	.31	
Ca 4227	1.72	.046	.11	.31		.29	.156	7.9	
Mn 4031	.055	.004	1.5 x 10 <sup>-6</sup>	.037		5.70	1.35	.38	
Ca <sup>+</sup> 3968	.35			.15	(1), .65	.74		11.8	
Al 3962	.12	.066	6 x 10 <sup>-5</sup>	.041	(1-4)	5.60	.167	1.86	
Ca <sup>+</sup> 3934	.69			.27	(1), 1.3	.30	1.22	5.5	
Fe 3859	.03	1.0	3 x 10 <sup>-6</sup>	.014	(30-100)	7.90	.185	1.05	
AlO 4844	.00125			.0185			3.5	21.7	
Si { UV, ozone shielded }		.64			(40) ?		2.6	520.0	
Mg {		.54			(15-100)				

\* The number of photons scattered per sec. by a sunlit atom, ion or molecule.

\*\* Typical measurements by optical and by ion mass spectrometric (the numbers in parentheses) methods.

† The table is described in detail in Section 3.4 of the text.

### 3.3 Gadsden's Antarctic Twilight Search for Trace Metal Constituents

A beginning in this direction of research was made by Gadsden (1969). He attempted to use the long Antarctic twilight (April-September 1966) to observe the emission lines of any metals that might be present. He searched for Al, Ca, Cr, Sr, K, Li, and Na. Na was the only specie that was detected. Upper limits were set on the column densities (or abundances) of all others. The results of the experiment are summarized in Table I.

### 3.4 The Significance of Table I

Table I presents a concise summary of our present observational knowledge of the alkali metal layers and of the E-region metal ion layer. It presents a comprehensive summarization of the feasibility of some current optical experiments that one may perform in order to detect upper atmospheric metals. Two kinds of optical experiments are considered, twilight photometry and laser radar. Relative abundances of metals in meteors, in sea water, and in the upper atmosphere are all listed together so that one may conveniently examine them and make quantitative comparisons. Such comparisons are useful in determining whether the primary origin of the atmospheric metals is meteoric or sea water or some combination of the two.

Table I is large and complex. This paragraph contains a detailed column-by-column description of its contents. The oscillator strengths in the third column are copied for the most part from Gadsden's (1969) paper. A value of  $f_c = 10^{-2}$  was assumed for AlO. Next this was corrected for the Franck-Condon factors for the A-X (0-0) band at 4844Å. It was also corrected for the subsequent dilution of the laser beam intensity on spreading it across a 1Å region including the bandhead and finally for the rotational population residing in this much of the branch. The other important metal monoxides FeO, MgO, SiO, NaO and LiO are believed to have no visible spectrum connected to the ground state. They are discussed more completely in Section 4.5 below. The relative abundances of the metals in sea water and meteors normalized to Na and Fe respectively are given in the fourth and fifth columns. The quantity  $g$ , listed in the sixth column is the number of visible photons scattered per second per molecule by a sunlit molecule, ion or atom. It is calculated for AlO for a 1Å region containing the A-X (0-0) bandhead. The column headed 'Typical Measurements' presents column densities of the species that have been observed either



by optical or ion mass spectrometric means. Ion mass spectrometer measurements are in parentheses, the smaller numbers that are given refer to quiet conditions and the larger to enhancements. Only Na has been measured both optically in the form of neutral Na and ion mass spectrometrically in the form of  $\text{Na}^+$ . Ca<sup>+</sup> has been measured both optically and ion mass spectrometrically. The upper limit on the column densities of the various species as found by Gadaden (1969) in his Antarctic twilight experiment are presented in the column titled 'Upper Limits'. The column headed 'Minimum Detectable via Twilight Photometry' gives the lower limit on the column density of a given species that one might expect to observe in an idealized experiment where one is assumed to be able to detect a minimum twilight intensity of 5 R. The lower limit on the column density thus detected is given by:

$$N = 5 \times 10^6/g$$

From the column headed 'Typical Measurements' one sees that in periods of enhanced activity one can expect column densities of  $\text{Al}^+$  of about  $4 \times 10^8 \text{ cm}^{-2}$ . This is concentrated in a layer of half width  $\approx 8 \text{ km}$  centered at  $\approx 95 \text{ km}$ . One might expect this to provide a lower boundary on the concentration of aluminum in the forms  $\text{Al}^+$ , Al, AlO, or  $\text{AlO}_2$ . (One might also expect the altitude profile of the sum of these components to be that of the ambient atmosphere.) It is clear that there should be detectable amounts of either Al or AlO or both present if not too large a fraction of the aluminum is in the form  $\text{AlO}_2$ . The minimum detectable column density of a given specie using current laser technology (Miranda, P. C.) capable of detecting a minimum of  $10^8 \text{ Na atoms/cm}^2$  is given in the column headed 'Minimum Detectable by Laser'. Order of magnitude improvements in the capability of laser radar can be expected in the future.

## Section 4

### THE EXPERIMENTS

#### 4.1 New Experiments Currently in Operation

4.1.1 Current Laser Experiments. Sandford and Gibson (1970) have reported the results of a laser radar study of the twilight and nighttime Na layers. The abundance is found to remain essentially constant throughout the night. They confirm that the seasonal variation and the existence of a steep top and bottom side scale height are present in the nighttime layer. Preliminary laser radar results obtained by Miranda (1971) are in essential agreement with those of Sandford et al. In addition they report numerous sightings of layers with secondary maxima. They notice with 5% correlation, a tendency for the Na abundance to increase by some 20% in a short time period (30 min) after the evening twilight layer is no longer sunlit.

Sandford et al. (1970) attribute the double maxima to patches of Na at slightly different altitudes moving rapidly by in a horizontal direction. B. McCormac (1971) has suggested that this effect could be due to erratic vertical movements of the layer in a time period short compared to the integration time of the electronics employed with the laser. Erratic vertical movements of sporadic E have been observed. The two hypotheses are not essentially contradictory.

It is hoped that by concurrently operating two lasers viewing different parts of the sky the moving patch hypothesis can be tested. With more powerful lasers it will be possible to verify the daytime diurnal variation. This check would be intrinsically free of Ring Effect contamination of course. One should also be able to use more powerful tuned dye lasers to look for a host of other trace constituents in the earth's atmosphere. These are listed in Table I described in Section 3.4.

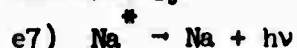
4.1.2 Donahue and Guenther currently have a satellite mounted filter photometer that looks horizontally at the Na layer. This kind of experiment should be able to measure the dayglow free from Ring Effect contamination. It can also record the world wide effects of disturbances such as large solar flares, sudden enhancements, nuclear blasts, etc. Currently the

experiment is mildly degraded by the Rayleigh scattered signal getting through the 27A bandpass filter. This broadband filter is employed because of the severe temperature extremes that the satellite encounters. Guenther (PC) states that this could be improved by installing on-board temperature control systems. The instrumental sensitivity is comparable to current Zeeman photometry in spite of the use of the broad band filter. They have also observed altitude profiles of the nighttime chemiluminescence of the Na layer.

These observations are quite interesting. They represent a measurement of the altitude dependence of some chemical form of excitation of Na. Srivastava and Shukla (1970) have suggested that the Chapman mechanism is mainly responsible for the Na nightglow emission. Briefly, this mechanism is



followed by



NaO is regenerated via



Using their rate constants, typical Na nightglow emission rates of 100 R and  $\langle \bar{O} \rangle \approx 4 \times 10^{10} \text{ cm}^{-3}$  above 70 km one finds upper limits for the column densities of NaO and NaO<sub>2</sub> above km of

$$N_c(\text{NaO}) \leq 6 \times 10^7 / \text{cm}^2$$

$$N_c(\text{NaO}_2) \leq 24 \times 10^7 / \text{cm}^2$$

As compared with typical Na column densities above this height of

$$N_c(\text{Na}) \approx 5 \times 10^9 / \text{cm}^2$$

The conclusion is that an insignificant portion of the Na inventory is in the form of NaO or NaO<sub>2</sub> above 70 km. It is possible that NaO<sub>2</sub> is unstable. This further supports the statement above regarding the Na inventory.

Obviously simultaneous nighttime measurements of the altitude profiles of the Na chemiluminescence by satellite photometry and of the Na number density by laser radar would provide data extremely pertinent to the chemistry of Na.

## 4.2 Future Experiments

### 4.2.1 Established Experimental Techniques

4.2.1.1 The established techniques include twilight photometry, daytime Zeeman photometry and rocket mounted photometers.

4.2.1.2 Twilight photometry should continue to be a useful tool for documenting the seasonal variation of the alkali metal abundances in various parts of the world. Layer structure can be determined to some extent using this technique. By comparing the data in the last four columns of Table I one should note that twilight photometry has not been pushed to its full potential for detecting the trace metals in the E-region.

4.2.1.3 The search for AlO via twilight photometry is also a prospect for this technique. Essentially it is just as feasible to search for AlO via the methods of twilight photometry as it is to search for Al (see Table I). The discovery of naturally occurring AlO in the upper atmosphere would constitute the first direct observation of any of the metal compounds that are supposed to provide the sink for metal species in the upper atmosphere. Even a negative result would be valuable. The inferred lower limit on the AlO abundance would provide a boundary condition for theories of the chemistry and dynamics of naturally occurring aluminum in the upper atmosphere. This experiment could be done immediately using standard techniques of twilight photometry that have been developed.

4.2.1.4 The future of Zeeman photometry depends on how well the Ring Effect contamination can be dealt with. Albano et al. are currently working on this problem. Zeeman photometry will provide an effective tool for documenting the seasonal and diurnal variation of alkali metal abundances provided that the Ring Effect can be dealt with or that it is found to be of negligible importance. It is hoped that Zeeman photometer data taken in the past can be reinterpreted to account for the Ring Effect if this is found to be necessary.

4.2.1.5 Rocket mounted photometric observations of the Na layer ~~should~~ be entirely supplanted by improved laser radar that will obtain the same kind of data (related to layer structure) more often and more cheaply. (See Section 4.2.2 below.)

#### 4.2.2 The Future of Laser Radar

4.2.2.1 Sandford et al. have convincingly demonstrated the value of the laser as an investigatory tool. Their laser investigation, though limited temporally and geographically, has provided more reliable data on the nighttime morphology and abundances, previously unknown, than exists to date on the daytime which has been studied for many years.

4.2.2.2 The development of improved laser radar is justified on the basis of what it should be able to do in obtaining daytime information concerning Na abundance and altitude profiles. A laser, operating all day, day after day, is equivalent to several rocket flights each day and capable of vastly increasing our knowledge of the morphology of the daytime layer.

4.2.2.3 The potential of laser radar for the investigation of Na has been established above. One may get some idea of the relative potential for the study of other species by laser radar vs. twilight studies by comparing the data in Table I regarding the upper limits on the column densities one may detect via the two techniques. It is clear that the lasers must be improved by at least two orders of magnitude in order to make laser radar a decisively better tool than twilight photometry. For the case of Li make it three orders of magnitude.

#### 4.2.3 The Future of Satellite Technology

4.2.3.1 Satellite mounted photometers in polar and equatorial orbits should be able to obtain all the data that one could possibly hope to have regarding the sunlit Na layer. The altitude profile of the nighttime Na chemiluminescence can also be measured by satellite photometry. The importance of simultaneous nighttime measurements of the altitude profiles of the Na chemiluminescence by satellites and the Na number density by lasers has been established in Section 4.1.2 above. Simultaneous measurements of the wind patterns and the metal ion layer would further enhance the experiment's value.

It may be possible that the sensitivity of the satellite mounted photometers can be developed to the point where the much fainter emissions of K and Li could be detected also. (Typically the ratio of the intensities of the light scattered in the upper atmosphere by Na, K, and Li is 300:6:5). It is not inconceivable that unmanned satellite instrumentation could be pushed to the point where some of the heretofore optically unobserved metal species listed in Table I might actually be detected.

4.2.3.2 The manned satellites forecast for this decade present a truly exciting prospect for research of all kinds. Sensitive ground based optical systems that have been developed over the years may now be operated from satellite platforms. Ultrasensitive IR and UV detectors as well as visible detectors may be employed.

A ground-based photometer capable of observing 5R in the twilight glow should be able to observe zenith-corrected intensities of at least .5R and perhaps as weak as .05R when scanning the horizon from a satellite platform. Two effects make this possible. The photometer will be able to view a much larger number of emitters by viewing the horizon. The integration time will be much longer. Hence for such a manned satellite mounted photometer the lower limits on the detectable abundances of various metal species as listed in the column headed 'Minimum Detectable via Twilight Photometry' in Table I may be reduced by a factor of at least 10 and possibly 100.

Technologically speaking the simultaneous operation of the most sensitive detectors available in the visible, IR and UV offers the most powerful way to try to measure the total inventory of several of the metal species in the E-region. This then should provide the data necessary to uniquely specify the source of metals in the upper atmosphere and also the chemistry and dynamics of their removal. (See Section 3.2 above.)

The deployment of such equipment on manned satellites is, of course, a question of economic priorities. One should note, however, that the atmospheric metal problem is only one of many problems that could be resolved by the rich data that such instrumentation could obtain.

A study aimed at precisely specifying the lowest detectable limit of the column densities of the various metal atoms, ions, and compounds that one might expect to observe with the most sensitive available detectors in the visible, IR and UV operating from a manned satellite would certainly be a worthwhile project.

An intrinsically valuable laboratory program aimed at a detailed documentation of the visible, IR and UV spectra of these species would naturally complement this study. The expense involved in the first of these projects would be virtually negligible.

#### 4.2.4 Rocket Mounted Detectors of all Kinds

4.2.4.1 Sensitive IR detectors scanning in the  $4\ \mu$  to  $40\ \mu$  range, mounted on rockets and looking in the horizontal direction may be able to detect some of the metal compounds. This requires laboratory studies of the vibration rotation spectra of the metal compounds suspected of being in the upper atmosphere. This experiment would be intrinsically valuable for detecting all atmospheric molecular trace constituents since the principal atmospheric constituents  $N_2$ ,  $O_2$  and A do not radiate in this part of the spectrum. The altitude profile of  $HNO_3$ , possibly important to mesospheric metal chemistry, could certainly be measured this way as could the altitude profiles of NO and  $N_2O$ . One could infer the eddy diffusion coefficient as a function of altitude from the water vapor mixing ratio that one could measure up to 90 km with a sensitive enough rocket mounted IR detector. One could also measure the topside ozone profile. Simultaneous measurements of the topside ozone and water vapor profiles would help to clarify the role of hydrogen reactants in the removal of ozone.

4.2.4.2 A feasibility study of rocket mounted filter or resonance cell photometers that could be used to search for E-region metals and metal ions would be worthwhile. This could include the UV shielded resonance emissions of  $Fe^+$  and  $Mg^+$ . This technique may be just as effective as ion mass spectrometry in measuring the altitude profile of the metal ion layers.

Table II  
Ozone Shielded UV Metal and Metal Ion Spectra

Element	$\lambda$	f	Trans
Mg	2852.13	1.81	$^1S - ^1P$
Mg	2025.82	.22	$^1S - ^1P$
Mg <sup>+</sup>	2795.53	.627	$^2S - ^2P$
Mg <sup>+</sup>	2802.7	.313	$^2S - ^2P$
Si	2518.3	1.64	$^3P - ^3P^0$
Si	2214.7	.55	$^3P - ^3D^0$
Fe	3440.61		$a^5D_4 - z^5P_3$
	3020.6		$a^5D_4 - y^5D_4^0$
	2983.57		$a^5D_4 - y^5D_3$
	2966.90		$a^5D_4 - y^5F_5$
Fe <sup>+</sup>	2585-2621		$a^6D - z^6D$
	2366-2413		$a^6D - z^6F$
	2327-2380		$a^6D - z^6P$
SiO	2345.		(0 - 0)



4.2.4.3 None of the ozone shielded UV emissions of any of the metals present in the E region (see Table II) have been detected by UV spectrometry. Pearce (1971) reports some observations of the earth's UV dayglow. The UV spectrometers that have been used, however, have sacrificed sensitivity in order to scan a very broad spectral range. UV spectrometers could certainly be designed and programmed to look for specific metal and metal ion emissions. A feasibility study aimed at prescribing the lowest detectable limits on the column densities of the species that one might hope to detect by using such UV spectrometers mounted on rockets would be worthwhile.

#### 4.2.5 The Metal Monoxides

A direct measurement of any metal monoxide in the mesosphere would be quite valuable. The role of NaO in the old chemical theory of the Na layer is a primary reason for this. Metal monoxides that radiate in the atmospheric IR window near  $11.5\mu$  (AlO, FeO, and LiO) are also interesting.

No visible spectra of the alkali monoxides have been reported. Nicholls (1967) has searched unsuccessfully for such spectra in shock tube experiments. FeO, MgO and SiO might be expected to occur rather abundantly in the upper atmosphere since  $\text{Fe}^+$ ,  $\text{Mg}^+$  and  $\text{Si}^+$  are the major E region metallic ions (see Table I, column F). The spectrum of SiO lies in the ozone shielded UV region. It is very similar to that of NO. Its observation has not been reported in the UV literature (Pearce, 1971). MgO exhibits a rich visible spectrum in singlet transitions. The ground state of MgO may be triplet however and as is the case for NaO, no spectrum of triplet MgO transitions has been reported. Nicholls suggests that the triplet ground state may be several thousand  $\text{cm}^{-1}$  lower than the singlet metastable ground state thus implying that virtually all MgO in the relatively cool upper atmosphere is in the invisible triplet ground state. The case for FeO is similar to that of MgO. It has a rich visible spectrum which is believed to be that of a metastable version of the molecule. Furthermore, the visible spectrum of FeO is less well known than that of some of the other metal oxides.

A sensitive rocket mounted horizontally scanning IR detector seems the best prospect for detecting upper atmospheric existence of

these species. This is especially true for FeO which radiates near  $11.5\mu$ ,  $\text{HNO}_3$  is the only obvious atmospheric specie that would produce a background in this wavelength region.

AlO does have a ground state connected visible spectrum. One sees from the columns titled 'Typical Measurements' and 'Minimum Detectable via Twilight Photometry' in Table I that a 5R twilight intensity in the A-X (O-O) bandhead could be produced by a column density of AlO that is comparable to column densities of  $\text{Al}^+$  that have already been detected ion mass spectrometrically.

With the projected advent of dye lasers three orders of magnitude better than current ones and tuned to the resonance lines and bands of Al and AlO one could perform an experiment in conjunction with rocket mounted ion mass spectrometers that would allow one to simultaneously measure altitude profiles of Al, AlO and  $\text{Al}^+$ . Since at 90 km  $\text{AlO}_2$  is assumed to be the only other aluminum containing reactant this experiment should be a large step towards allowing one to uniquely solve the problem of the chemical dynamics of aluminum in the upper atmosphere. One should be cautious however in view of the fact that no production of AlO has been observed in either TMA releases or grenade explosions below 90 km. Furthermore, the relatively small dissociation energies of the metal monoxides argues against any of them comprising a major portion of their respective metal inventories. The fact that NaO above 70 km is a minor portion of the Na inventory (Section 4.1.2 above) supports this argument.

#### 4.2.6 Wind Patterns

Wind induced  $\mathbf{V} \times \mathbf{B}$  forces play a major role in many of the Na layer models (Section 2.2). It would be useful to perform simultaneous measurements of wind patterns and of the Na layer in order to assess the actual role of these forces in the formation and maintenance of the Na layer.

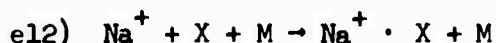
#### 4.2.7 IR Tracked Chemical Releases

Releases of Na vapor have been made in order to elucidate the Na chemistry. Not much was learned regarding the Na chemistry due partly to difficulties in the interpretation that were caused by the extreme optical thickness and complicated geometry of the vapor trails. These experiments could be repeated with lithium for example and with the vapor

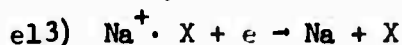
clouds observed in the IR as well as in the visible. The IR data would be directly related to the chemistry since it could conceivably record the formation of LiO and LiO<sub>2</sub> as a function of time. The LiO and LiO<sub>2</sub> clouds should be optically thin and at the worst only moderately optically thick in the IR region. The fundamentals of LiO and LiO<sub>2</sub> have been measured and reported in the literature (Andrews, 1969; White et al., 1963). Release experiments of this type would fit quite naturally into Lockheed's present program.

#### 4.2.8 The Role of Ion Clusters in Metal Chemistry

Keller and Beyer (1971) have recently established the importance of an ion clustering mechanism for the conversion of Na<sup>+</sup> to Na. The process is



followed by



where M is any third body and X may be CO<sub>2</sub>, O<sub>2</sub>, or N<sub>2</sub>.

The role of ion clusters in the conversion of metals into metal compounds should be investigated. This line of research has successfully identified some important processes for the conversions of Na<sup>+</sup> to Na.

J. E. Evans suggests that NaHCO<sub>3</sub> or NaNO<sub>3</sub> may form in the water cluster ions below 85 km for example. The observation of mesospheric HNO<sub>3</sub> (Murray, 1969) lends some credence to this hypothesis.

## 5. CONCLUSIONS

The many experiments suggested in this article have ranged from simple twilight photometry to the extravagant concept of batteries of the finest optical equipment available scanning the Earth's horizon in all portions of the spectrum from manned satellites. And although experiments of the latter variety may never be implemented, studies aimed at assessing their full capabilities would be extremely interesting and would cost virtually nothing. Ideally this study should assess the impact of such an experiment on all phases of earth-space physics.

All of the experiments discussed in this paper are valuable in that they will obtain data pertinent to the E-region metal problem. The experiments are listed below in three classes. Experiments that could be immediately implemented and that are feasible in both a technological and economic sense constitute the first class. Experiments that are technologically sound but rather expensive make up the second class. Inexpensive studies to assess their capabilities could be conducted. Experiments that need further study to determine whether they are technologically sound make up the third class.

The first class includes: 1) The attempt to detect various metal species and especially AlO using standard twilight photometry; even negative results from this experiment would be valuable. 2) The documentation of both the night glow and the sunlit Na layer by simple filter photometers mounted in standard unmanned satellites in orbits of various inclinations. 3) The world wide deployment of slightly improved laser radars capable of night and day time observations of the Na layer. 4) A statistically significant number of simultaneous night time measurements of the Na chemiluminescence altitude profile and the Na concentration as a function of altitude by satellite photometry and laser radar. This would represent the optimum utilization of these technologies in obtaining data pertinent to the Na chemistry in the upper atmosphere. The simultaneous measurement of wind patterns, in conjunction with measurements of the Na layer are also desirable. 5) Theoretical and laboratory studies of the formation of metal compounds in an E-region environment with special emphasis placed on the role of ion clusters. 6) Chemical releases of the most interesting metals tracked in both the visible and IR. And finally 7) laboratory documentation of the complete spectrum of all the metal compounds that are suspected to be in the upper atmosphere.

The Li problem merits special attention. Li emissions are relatively weak and have been detected to date exclusively by twilight photometry. Order of magnitude improvements in the methods of laser radar, Zeeman photometry and photometry from unmanned satellites are necessary in order to render these feasible for the observation of the naturally occurring Li. On the other hand data obtained by twilight photometry shows that the seasonal variation in column densities and in the altitudes of the evening-morning twilight layer are virtually identical for the two alkalis Li and Na. Hence it is possible that all the data that one could obtain on Na via the experiments described in this paper would apply directly to the Li problem. Li releases could also be used to obtain information regarding chemistry. Very large twilight releases tracked in the visible, the IR, by conventional radar and by laser radar could be made. Laser radar would allow one to monitor the Li inventory during twilight and into the night. Chemiluminescence providing direct information on Li chemistry could be observed simultaneously. The chemical removal rate of Li as a function of altitude could be obtained by releasing the Li clouds at various altitudes and recording the decay times corrected for the effect of ionization. Release obtained data concerning the chemistry of Li, Cs and Ba have been reported (Gault and Rundle, 1966; Pressman et al., 1960; Föppl et al., 1967).

There is just one experiment in the second class. This involves a manned satellite employing scientific equipment of all kinds. Technologically the equipment should be comparable to or better than the best current earth bound laboratory equipment. The general scientific potential of such an experiment is virtually unlimited.

Experiments in the third class are: 1) The search for trace metal constituents by improved ground based laser radar (see Table I) or by lasers operated in the horizontal direction and carried right up to the metal layer on rockets. Such rocket mounted lasers could conceivably operate in the ozone shielded region of the spectrum. 2) Sensitive rocket mounted IR detectors looking in the horizontal direction. 3) Rocket mounted filter or resonance cell photometers looking in a horizontal direction for emissions from the various metal species. And finally 4) UV spectrometers programmed specifically to look for the ozone shielded emissions of various E-region metals and metal ions.

## REFERENCES

- Albano, J., J. E. Blamont, M. L. Channen, and M. Petitdidier, Observations of the Dayglow at the Resonance Wavelengths of Sodium and Potassium. Seasonal and Diurnal Variation., *Ann. Geophys.* 26, p. 151, 1970
- Andrews, L., Infrared Spectrum, Structure, Vibrational Potential Function, and Bonding in the Lithium Superoxide Molecule  $\text{LiO}_2$ , *J. Chem. Phys.* 50, pp. 4288-99, 1969
- Donahue, T. M. and R. R. Meier, Distribution of Sodium in the Daytime Upper Atmosphere as Measured by a Rocket Experiment, SRCC Report No. 36, University of Pittsburgh, 1967
- Föppel, H., G. Haerendel, L. Haser, P. Lutjeus, R. Lust, T. Melzner, B. Meyer, H. Neuss and E. Rieger, Artificial Strontium and Barium Clouds in the Upper Atmosphere, *Planet. Space Sci.* 15, 357, 1967
- Gadsden, M., Metallic Atoms and Ions in the Upper Atmosphere, *Ann. Geophys.* 26, pp. 141-51, 1970
- Gadsden, M., Antarctic Twilight Observations, 1. Search for Metallic Emission Lines, *Ann. Geophys.* 25, pp. 667-77, 1969
- Gault, W. A. and H. N. Rundle, The Decay Over Long Distances of Rocket-Released Lithium Due to Diffusion, Winds and Chemical Reactions, *Can. J. Phys.* 44, 1099, 1966
- Griniger, J. F. and J. Ring, Anomalous Fraunhofer Line Profiles, *Nature* 193, p. 762, 1962
- Hanson, W. B. and J. S. Donaldson, Sodium Distribution in the Upper Atmosphere, *J. Geophys. Res.* 72, p. 5513, 1967
- Hunten, D. M., Airglow - Introduction and Review, *The Radiating Atmosphere* (Proceedings of the Summer Advanced Study Institute, *Aurora and Airglow*, 1970, ed. by B. M. McCormac), D. Reidel Publishing Co., Dordrecht, Holland, 1971
- Hunten, D. M., Surface Albedo and the Filling In of Fraunhofer Lines in the Day Sky, *Astrophys. J.* 159, p. 1107, 1970
- Hunten, D. M., Spectroscopic Studies of the Twilight Airglow, *Space Sci. Rev.* 6, pp. 493-573, 1967
- Hunten, D. M. and W. L. Godson, Upper Atmospheric Sodium and Stratospheric Warmings at High Latitudes, *J. Atmos. Sci.* 24, pp. 80-87, 1967
- Hunten, D. M. and L. Wallace, Rocket Measurements of the Sodium Dayglow, *J. Geophys. Res.* 72, p. 69, 1967

- Keller, G. E. and R. A. Beyer,  $\text{CO}_2$  and  $\text{O}_2$  Clustering to Sodium Ions, J. Geophys. Res. 76, pp. 289-91, 1971
- Llewellyn, E. J. and W. F. J. Evans, The Radiating Atmosphere (Proceedings of the Summer Advanced Study Institute, Aurora and Airglow, 1970, ed. by B. M. McCormac), D. Reidel Publishing Co., Dordrecht, Holland, 1971
- Lumenello, T., J. Davis and J. Freedman; SECEDE I Photographic and Spectrographic Data Reduction, EG&G Tech. Rep. B-4088
- Murcray, D. S. and F. H. Murcray, W. J. Williams, T. G. Kyle, A. Goldman, Variation of the Infrared Solar Spectrum Between  $700\text{ cm}^{-1}$  and  $2240\text{ cm}^{-1}$  with Altitude, App. Optics 8, pp. 2519-2536, 1969
- Narcisi, R. S., Processes Associated with Metal-Ion Layers in the E region of the Ionosphere, Space Res. VIII, pp. 360-369, North-Holland Publishing Co., Amsterdam
- Nicholls, R. W., Table of the States and Spectra of the Metallic Monoxides, Appendix A in DASA Report 1917-4, Thermal Radiation Phenomena, Excitation and Nonequilibrium Phenomena in Air, by R. K. Landshoff and J. L. Magee, edit. by J. L. Magee and H. Aroeste, 1967
- Pearce, J. B., Some Observations of the Earth's Ultraviolet Dayglow, The Radiating Atmosphere (Proceedings of the Summer Advanced Study Institute, Aurora and Airglow, 1970, ed. by B. M. McCormac), D. Reidel Publishing Co., Dordrecht, Holland, 1971
- Pressman, J., F. F. Marmo and L. M. Aschenbrand, Low Altitude Study, Release of Cesium at 69, 82, and 91 km, Planet. Space Sci. 2, pp. 228-37, 1960
- Rundle, H. N., Dayglow and Twilight Excitation Mechanism for Airglow, The Radiating Atmosphere (Proceedings of the Summer Advanced Study Institute, Aurora and Airglow, 1970, ed. by B. M. McCormac), D. Reidel Publishing Co., Dordrecht, Holland, 1971
- Sandford, M. C. W. and A. J. Gibson, Laser Radar Measurements of the Atmospheric Sodium Layer, J. Atmos. and Terr. Phys. 32, pp. 1423-1430, 1970
- Srivastava, A. N. and R. V. Shukla, Excitation Mechanism of Na-D Lines in the Nightglow, Ann. Geophys. 26, pp. 501-504, 1970
- Sullivan, H. M., Some Unusual Red Twilight Emissions, Ann. Geophys. 26, pp. 161-166, 1970
- White, D., K. S. Seshadri, D. F. Dever, D. E. Mann and M. J. Linevsky, Infrared Spectra and the Structures and Thermodynamics of Gaseous  $\text{LiO}$ ,  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{O}_2$ , J. Chem. Phys. (USA) 39, pp. 2463-73, 1963
- Young, J. M., C. Y. Johnson and J. C. Holmes, Positive Ion Composition of a Temperate-Latitude Sporadic E Layer as Observed During a Rocket Flight, J. Geophys. Res. 72, p. 1479, 1967