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NONR 4222 (01)  
ARPA ORDER #125, AMEND #8

TECHNICAL REPORT # 2  
TO  
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QUANTITATIVE STUDIES BY OPTICAL SPECTROSCOPY OF  
ENERGY EXCHANGE MECHANISMS IN SIMPLE GASES AND SOLIDS

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QUANTITATIVE STUDIES BY OPTICAL SPECTROSCOPY OF  
ENERGY EXCHANGE MECHANISMS IN SIMPLE GASES AND SOLIDS

Abstract

Emission studies have continued in fast flow systems of nitrogen energized in a microwave discharge.

By changing parameters of pressure, temperature, and mixture, silicon tetrahalides added after the discharge have produced two electronic systems of SiN, and two separate, unidentified emitters in the green and in the orange spectral regions. Addition of CO<sub>2</sub>, N<sub>2</sub>O and CO has shown near infra-red emission of these molecules, caused by transfer of vibrational energy from the ground electronic state of molecular nitrogen. To further the understanding of the N<sub>2</sub><sup>+</sup> emission observed in some afterglows, a detailed perturbation calculation for the v = 1 level of the B<sup>2</sup>Σ state and the v = 11 level of the A<sup>2</sup>Π has been undertaken.

A new set of studies in a well-behaved plasma produced by means of a brush cathode has been undertaken. Spectroscopic, electron probe, and voltage-current measurements are being made in hydrogen and in hydrogen-helium mixtures at pressures near 1 mm Hg.

The condensed phase studies of molecular solids has not had any significant results.

A review article on "Flame Kinetic Studies" is being prepared for publication in an Academic Press, Inc. series on "Methods in Experimental Physics", Volume VIII entitled "Atomic Physics".

EMISSION FROM THE REACTIONS OF VOLATILE SILICON COMPOUNDS WITH  
ACTIVE NITROGEN

K. Schofield

Abstract

Using an atomic flame technique, more detailed studies of some of the initial findings, resulting from the addition of volatile silicon compounds to active nitrogen, have been pursued. These studies have centered on photographic and high resolution photo-electric emission detectors in the 2000 - 9000 A region, of some of the interesting phenomena and new systems previously reported by the author.

Efforts have been made to observe any spectral dependences on the system's variables, such as working pressure, flow rate, concentration of additive, etc. Following the preliminary findings the additives used have been  $\text{SiCl}_4$  and  $\text{SiBr}_4$ , the former giving rise to two systems of SiN and a yet unassigned green system, whilst the latter gives an interesting gaseous orange system emission, as yet unreported. Established systems have been studied in detail, whilst efforts are being made, with the newly observed systems, to correctly assign them to the emitting molecules, establish the electronic transitions involved, carry out a vibrational numbering of the individual bands and observe the rotational structure of any bands of sufficient intensity for such an analysis.

By adding  $\text{GeCl}_4$  to discharged nitrogen a spectrum of GeN previously unreported has been obtained.

Objective

Recent double-resonance experiments involving the  $A^2\Pi$  and  $B^2\Sigma$  electronic states of CN have been successful. Since molecules as SiN,  $\text{N}_2^+$ ,  $\text{CO}^+$  etc. likewise have nine valence electrons, these are basically identical having the same kind of electronic states

spaced in a similar manner. Consequently by observing the perturbations in the  $B^2\Sigma - X^2\Sigma$  system of SiN as a function of pressure, added inert diluent, flow rate, etc., information as to the nature of the collision processes involved, the rates and mechanisms for populating and depopulating the rotational, vibrational and electronic levels may be derived. If as with CN, population inversions are obtained, then the feasibility of inducing microwave transitions between levels near the perturbed levels can be established.

#### Program

1. Observe the violet spectrum of SiN.

The  $B^2\Sigma - X^2\Sigma$  SiN violet bands are fairly well established and those observed have been assigned to the particular vibrational transitions which they represent. A search is to be made for all these bands and possibly others which would be fitted into the general scheme.

Measure relative intensities and observe as to whether these are a function of any variable of the system.

Using the strongest bands, observe the rotational structure and note any rotational perturbations present. These regions of the perturbations are to be studied in detail as to any effect due to pressure, flow rate, etc.

2. Other systems of SiN

Look in the  $1\ \mu$  region for evidence of the unobserved yet expected "Red"  $A^2\Pi - X^2\Sigma$  system of SiN.

The other system of SiN observed by Mulliken and assigned not very confidently to the  $C^2\Pi - A^2\Pi$  transition has always been observed as very weak emission, giving double-headed bands as compared to the single headed  $^2\Sigma - ^2\Sigma$  violet bands. It has been found, however, that when the flowing atomic flame system is passed through a cold (liquid  $N_2$ ) trap the resulting blue glow from the trap contains these Mulliken bands, greatly increased in intensity relative to the B - X violet bands, and they become

readily observable. The bands observed by Mulliken are to be searched for and a check made on their vibrational assignments, and consequently a check as to whether the upper state of the transition is  $C^2\Pi$  or whether the transition observed is the  $B^2\Sigma - A^2\Pi$ .

A new type of cold trap is to be used to facilitate observation and make it possible to study the emission as a function of wall temperature, possibly down to  $4^{\circ}\text{K}$ .

3. The newly observed 'orange system' in the 5700-7500 A region, produced by the addition of  $\text{SiBr}_4$  to active nitrogen and observed as a gaseous emission rather than the known orange NBr emission, which can occur on the walls of the reaction vessel, is to be studied in more detail so that various assignments can be made.

4. Similarly the 'green system' resulting from  $\text{SiCl}_4$  and active nitrogen is of unknown origin. It appears in the 5150 - 6000 A region and will be studied in as complete a spectroscopic manner as the intensity permits.

5. Investigate the spectral emission resulting from the addition of  $\text{GeCl}_4$  to active nitrogen. A strong turquoise emission results and a clearly banded system is observed in the 4200 - 5200 A region which can possibly be safely assumed to arise from the  $B^2\Sigma - X^2\Sigma$  transition of GeN owing to the similar nature GeN must have to CN, SiN and other nine valence electron diatomic molecules.

Before an analysis and complete assignments can be made in this case, owing to the fact that natural germanium exists with the following masses and abundances,

70 (20.5%), 72 (27.5%), 73 (7.8%), 74 (36.6%), 76 (7.8%)

which complicates matters too much, a relatively pure isotopic sample of  $\text{GeCl}_4$  is required containing only one or possibly two of the isotopes.

#### Summary of Progress

1. Violet Spectrum of SiN.  $B^2\Sigma - X^2\Sigma$ .

The  $^2\Sigma - ^2\Sigma$  system lies in the 3780 - 5260 A region, bands

with  $\Delta v = 0, +1$  being strong compared with the other sequences, these strong bands lying between 4000 - 4300 A.

So far, the 3650 - 7000 A region has been carefully scanned for all bands of this system, those previously reported have been picked out and measurements are now being carried out on the remaining unknown features to see if any belong to this same system. The scan will soon be expanded down to 2000 A and up to 10,000 A for completion.

As to whether relative band intensities, and hence vibrational populations, vary with working pressure and other conditions, has not yet been entirely settled and more measurements at various settings are required.

The (1,1), (2,2), (3,3), (4,4), (5,5), and (4,3), (5,4), (6,5), (7,6) bands are intense enough to be studied in detail, particularly for the presence of perturbations. The only observed perturbations occur in the  $v' = 4$  bands at the rotational levels  $J = 14, 19$  and  $21$ , showing well in the P branch of the (4,4) and (4,3) bands.

A preliminary observation of these perturbations has shown behavior apparently dissimilar to CN as regards the effect of working pressure. In the 10-30 mm Hg pressure range no definite evidence has yet been obtained to show that the perturbation is a function of pressure. One scan at 4 mm pressure did seem to affect the P(22) line but until repeated is unreliable. More scans of the perturbation region at various pressures will be made over as large a pressure range as possible. Using standard perturbation methods it is hoped that some information as to the perturbing state can be obtained, the most probable one being the  $A^2\Pi$ .

"Red" system of SiN  $A^2\Pi - X^2\Sigma$

No evidence for its occurrence has yet been obtained but a further attempt to observe it is to be made soon.

By considering all the established 9 valence electron diatomic molecules and noting the relative positions of the known  $B^2\Sigma$ ,

$A^2\Pi$  and  $X^2\Sigma$  states, general trends can be seen. It can be concluded from such an analysis that whilst CN and  $N_2^+$  are almost identical and show similar B-X and A-X transitions, SiN ought to be almost identical to CP whose levels are known. For CP, however, it is the  $B^2\Sigma - A^2\Pi$  transition and the B - X transition which are observed so it might be expected that observed transitions of SiN would be a  $B^2\Sigma - X^2\Sigma$  and a  $B^2\Sigma - A^2\Pi$ . An estimate of the region in which one might expect the A-X transition can be made. The (0,0) band would fall probably around 14,000 Å. Observation is planned out to 10-11,000 Å in the hope that some bands at the short wavelength end of the system may be picked up.

Mulliken<sup>2</sup> (1925) reported observing a very weak system of double-headed bands along with the strong  $B^2\Sigma \rightarrow X^2\Sigma$  violet bands of SiN. He reported bands from 3180 - 5620 Å and attempted a vibrational assignment, perhaps a little doubtful, from which values for  $\omega_e$  and  $\omega_e x_e$ , the vibrational frequency and anharmonicity constant for the upper and lower electronic states of this transition were derived. The  $\omega_e$  and  $\omega_e x_e$  obtained for the upper state differ greatly from those had by Jenkins and Laszlo<sup>3</sup> for the  $B^2\Sigma$  state. Consequently, unless Mulliken's vibrational assignment is incorrect, the observed transition appears to be a C -  $A^2\Pi$  one.

Since Mulliken's initial observation of this weak system, no other reports on the system have been made. A method has been found, however, to enhance the intensity by passing the flowing gases into a cold liquid  $N_2$  trap. This trap emits a blue glow which consists of the  $^2\Sigma - ^2\Sigma$  system along with the double-headed Mulliken's bands. The region 3600 - 7100 Å has been carefully scanned. All the bands in this region reported by Mulliken have been observed whilst new ones above 5620 Å are observed. The region 2000 - 3600 Å still needs to be covered, so that as many new bands as possible can be observed, to check the vibrational assignments previously made. This work should establish this

system more definitely.

The relative intensities of these double headed bands are to be compared at liquid  $N_2$  temperature, in the trap, with the very weak emission from the room temperature atomic flame. A more versatile trap is to be tried so that its temperature may be varied to see if wall temperature is an important factor in enhancing the doubled headed bands. To check any population changes, the C - A and B - X violet bands will be compared as to variation of intensities of the bands of one system relative to the other.

### 3. "Orange System"

The orange system, the emission from an orange colored afterglow resulting from adding traces of  $SiBr_4$  to discharged nitrogen, has so far been photographed at low dispersion. Plates showing higher dispersion and resolving power are to be taken as also are photoelectric tracings, in an attempt to assign the emission to the correct emitting molecule. Possibilities are  $Si_2$ ,  $Br_2$ ,  $SiBr$ ,  $SiN$  and  $NBr$  and since bromine has a 50/50 natural isotopic mixture it should not be too difficult to make a correct assignment. Band wavelengths will be measured and a standard spectroscopic treatment carried out for the system.

### 4. "Green System"

As with 3 above, this system has been similarly treated and is due for further study in the near future. It arises through adding a larger than usual amount of additive,  $SiCl_4$ , to active nitrogen and for this reason is expected to arise from  $SiCl$  or  $NCl$  molecules. The natural isotopic nature of the reactant again should facilitate spectroscopic analysis.

### 5. $B^2\Sigma - X^2\Sigma$ System of $GeN$ ?

As listed in the proposed program of work, the turquoise afterglow obtained by mixing a trace of  $GeCl_4$  to active nitrogen is, through its similarity to the usual 'blue'  $B^2\Sigma - X^2\Sigma$  systems of 9 valence electron molecules, most probably such a transition for  $GeN$ .

The spectrum is too complicated to work with at present owing to the five relatively abundant isotopes naturally occurring. Isotopically pure GeO is purchasable, however, so that volatile  $\text{GeCl}_4$  can be prepared. If the expected simplification of the spectrum results, a very full spectroscopic study of GeN could then be pursued.

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#### Footnote

Through the interest of H. P. Broida and K. Schofield in the general field of flames and combustion, it has been agreed that they will contribute an article entitled "Flame Kinetic Studies" to be published next year by Academic Press, Inc., N. Y. in their series, "Methods of Experimental Physics". It will appear in Vol. VIII "Atomic Physics".

Time was devoted to writing this survey type article this past summer. A brief abstract of the general contents is outlined below.

The purpose of the article is to outline the experimental techniques that have been developed in the last decade or so, which make rate constants and reaction collision cross sections attainable from flame kinetic studies. Besides discussing basic apparatus and types of flames being studied at present, advantages and disadvantages of choosing to work at high, medium or low pressures are considered.

All the methods of obtaining flame composition are listed

and then the specialized techniques pertaining to the individual systems are outlined. The aim of the chapter is to cover not only bi- and termolecular reactions of neutral species but also those of charged species which can occur in flames, that is, ion-molecule and ion-electron reactions are included.

Results which have so far emerged from these techniques are analysed and compared internally, besides externally with values obtained from completely different techniques.

### III.

## POPULATION INVERSIONS IN THE $B^2\Sigma$ STATE OF $N_2^+$

J. L. Dunn

#### Abstract

A detailed perturbation calculation on the mutual interaction between the  $v = 1$  level of the  $B^2\Sigma$  state and the  $v = 11$  level of the  $A^2\Pi$  state of  $N_2^+$  is nearly completed. Data on the magnitude of the level separations are available for use in the perturbation calculations which will allow calculation of the microwave transition probabilities.

#### Objective

Quantitative measurements of separations and relative intensities of the perturbed levels in the  $B^2\Sigma$  state of  $N_2^+$  and methods for producing population inversions in these levels are desired. By measuring relative intensities of the rotational, vibrational, and electronic transitions as a function of pressure, temperature, and inert diluent, it should be possible to formulate a kinetic model which describes the excitation and relaxation mechanisms for the perturbed levels of interest. In this way, values for radiative lifetimes, relative populations, and collisional relaxation times can be obtained. Employing a standard quantum-mechanical perturbation calculation and using the measured values of the level shifts, values for the microwave transition probabilities between perturbed levels can be obtained. An extension of these problems is to determine the feasibility of possible microwave double resonance experiments.

#### Program

1. Perform quantitative measurements of the perturbed level shifts in the  $(1,n)$  bands of the  $B^2\Sigma - X^2\Sigma$  transition. With the existing facilities, attempt to observe and label the complementary perturbation originating in the  $v = 11$  level of the  $A^2\Pi$  state as

obtained in the  $A^2\Pi - X^2\Sigma$  transition. From the level shifts, calculate the microwave transition probabilities.

2. Investigate the pressure dependence of possible mechanisms which could affect the relative populations, radiative lifetimes, and collisional relaxation times of the perturbed levels.

3. Measure relative intensities of the perturbed, unperturbed, and extra lines as a function of pressure, temperature, and inert diluent. With this information, formulate a kinetic model for the competing processes from which values for the relative populations, radiative lifetimes, and collisional relaxation times can be obtained.

4. If feasible, attempt to obtain microwave spectra among the perturbed and neighboring unperturbed levels by the microwave - optical technique (double resonance) to determine the hyperfine structure and the dipole moment of the electronically excited states.

#### Summary of Progress

A detailed perturbation calculation on the mutual interaction of the nearly degenerate  $v = 11$  level of the  $A^2\Pi$  state and the  $v = 1$  level of the  $B^2\Sigma$  state is nearly complete. This method follows closely the calculations carried out by Radford<sup>1</sup> on the isoelectronic molecule CN. The values of the perturbing matrix elements, level shifts, and the hybrid eigenfunctions (linear combination of unperturbed eigenfunctions) will be used to calculate the microwave transition probabilities. In the rotational structure of the (1,0), (1,1) and (1,2) bands of the  $B^2\Sigma_v - X^2\Sigma_g^+$  transition, the anomalous multiplet splitting observed by Coster and Brons<sup>2</sup>, with a maximum occurring at  $J = 13\frac{1}{2}$ , is well resolved using a double-pass 0.75 meter monochromator of the Fastie-Ebert type in the 2nd order with a 1200 line/mm grating and 6  $\mu$  slit widths. In addition to the known splitting an additional resonance type multiplet splitting was observed, with a maximum occurring at  $J = \frac{1}{2}$ , and whose level displacements were approximately one order of magnitude smaller than the perturbation occurring at

$$J = 13\frac{1}{2}.$$

### Future Plans

As the perturbation calculations are completed and values for the level separations and microwave transition probabilities are obtained, one phase of the problem will be completed. There remains the quantitative study of the effect of pressure and temperature on the relative intensities of the unperturbed, perturbed, and extra lines of the  $v' = 1$  levels of the  $B^2\Sigma_u^+ - X^2\Sigma_g^+$  transition. In order to obtain information about the relative populations of the perturbed levels, the radiative lifetimes, and the collisional relaxation times, relative intensity measurements of the perturbed, unperturbed and extra lines will be undertaken in detail.

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#### IV.

### VIBRALUMINESCENCE OF CO<sub>2</sub>, N<sub>2</sub>O, AND CO IN ACTIVE NITROGEN

E. L. Milne\* and J. L. Dunn

#### Abstract

Addition to a stream of active nitrogen, of CO<sub>2</sub>, N<sub>2</sub>O or CO causes near infrared emission corresponding to the vibrational fundamentals of these added molecules. Excitation of these infra-red active gases was studied in the Lewis-Rayleigh, orange and pink afterglows of nitrogen. The energy source of the excitation was determined to be vibrationally excited molecules of N<sub>2</sub>(X <sup>1</sup>Σ<sub>g</sub><sup>+</sup>).

#### Objective

"Vibraluminescent processes," or collisional processes in which energy is transferred from a vibrationally excited molecule to a secondary molecule, resulting in the emission of radiation, have not had much systematic study. These studies will use a microwave discharge in a fast flow system to produce vibrationally excited molecules and the vibraluminescent reactions will be sought in the region after the discharge and the collision cross-sections measured.

#### Program

1. In a qualitative manner, search for infra-red emissions obtained with the addition of infra-red active molecules to active nitrogen.
2. Vary the relative concentration of atomic nitrogen and vibrationally excited nitrogen to determine the energy process.
3. For systems which produce radiation, obtain high resolutions (as high as intensities permit) emission spectra at various

positions along the flow stream. From these spectra, determine the time variation of vibrational and rotational populations ("temperatures").

4. Using the infra-red emitters as probes, study the vibrational quenching effects caused by non-emitters.

#### Summary of Progress

In the initial experiments prepurified  $N_2$  was used in a fast flow system, in which an electrodeless discharge was maintained in a de Laval nozzle (1 mm orifice) in a 13 mm o.d. Pyrex tube. The discharge was powered by a 2450 Mc/sec, 125 watt magnetron supply coupled to a  $1/4$  wave coaxial cavity.

Addition of small amounts of  $CO_2$  after the discharge caused strong quenching of the  $N_2$  pink afterglow<sup>1</sup> and produced strong emission in the  $CO_2$  4.3 $\mu$  band. The  $CO_2$  4.3 $\mu$  radiation was also produced strongly in the  $N_2$  orange afterglow which precedes the pink region and less strongly in the Lewis-Rayleigh afterglow. The peak of the  $CO_2$  emission was shifted toward the long wavelength side of the 4.3 $\mu$  atmospheric absorption bands.

Since the products of a nitrogen discharge include a mixture of N atoms, vibrationally and electronically excited molecules, and ions, a series of experiments was designed to distinguish between these possibilities as the source of the  $CO_2$  excitation. High purity He and Ar were pumped through a discharge in the nozzle. The addition of  $CO_2$  to these energetic gases<sup>2,3</sup> failed to produce any detectable infrared excitation.

Discharged  $N_2$  and mixtures of  $N_2$  in He or Ar were passed through a glass wool plug to deplete the concentration of vibrationally excited nitrogen ( $N_2^\dagger$ )<sup>4</sup> and produce mixtures with enhanced  $[N] / [N_2^\dagger]$  concentration ratios. NO was added to these gases just upstream of the reaction chamber to produce controlled amounts of  $N_2^\dagger$ <sup>4,5</sup>. Addition of NO always produced an increase in the intensity of the  $CO_2$  radiation. Generally, the increasing 4.3 $\mu$  band intensity reached maximum at or near the end-point

of the NO titration. Hence,  $N_2$  rapidly exchanges vibrational energy with  $CO_2$  while N-atoms have little or no effect in the excitation of  $CO_2$ .

For both the  $4.3\mu$   $CO_2$  and  $4.5\mu$   $N_2O$  bands, the emission generated in active nitrogen was shifted to longer wavelengths than was anticipated for room temperature bands. When excited in the Lewis-Rayleigh afterglow, these band peaks appeared near  $2280\text{ cm}^{-1}$  and  $2180\text{ cm}^{-1}$  respectively. When excited in the  $N_2$  "pink" afterglow, they appeared near  $2270\text{ cm}^{-1}$  and  $2170\text{ cm}^{-1}$ . The shift to longer wavelengths indicates excitation of high vibrational levels in the  $\nu_3$  modes of  $CO_2$  and  $N_2O$ .

Recent experiments show that  $N_2$  vibrational energy also is exchanged with CO leading to strong emission in the CO band near  $4.7\mu$ . Moreover, vibrationally excited CO has been formed in the afterglow of a discharge through CO.

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## THE BRUSH CATHODE PLASMA IN HYDROGEN

G. A. Woolsey

Abstract

The discharge in hydrogen at pressures near 1 mm Hg, obtained using a brush cathode, appears similar to that in helium.<sup>1</sup> It consists of a narrow relatively dark region adjacent to the cathode, together with a negative glow which extends beyond a ring anode. Stark effect measurements of the electric field in the dark region show almost the entire tube voltage ( $\sim 2\text{kV}$ ) to be across this space. Consequently, a uniform electron beam is generated with energy of the order of 2 keV, which accounts for the negative glow extending one or two orders of magnitude further than that in a normal glow discharge. Probe measurements, together with the fact that it is field-free, show the negative glow to be a plasma. Attempts to measure charge-carrier concentrations spectroscopically have so far been unsuccessful, due to the low positive ion densities ( $\sim 10^{10} \text{ cm}^{-3}$ ) in the plasma.

Objective

The well behaved helium plasma formed in a brush cathode discharge<sup>1</sup> suggests the desirability of extending this technique to other gases. It has been decided to study the mechanism and properties of the hydrogen brush cathode plasma, and in particular, to investigate the possibility of using the Balmer or other hydrogen series, and its associated continuum, in a spectroscopic study of plasma parameters. In addition to the use of hydrogen plasma, brush cathode studies will be made of other pure gases including argon, nitrogen, and perhaps oxygen.

Program

1. Obtain a hydrogen brush cathode plasma, sufficiently ionised

to allow observation of the Balmer series limit, and hence measurement of charge carrier concentrations<sup>2,3</sup> and electron temperature<sup>3</sup>. Compare these measurements to those made with a conventional single probe.

2. Failing this, use mixtures of hydrogen and helium in an effort to increase the degree of ionisation, and thus allow the Balmer series to become a useful method of study.
3. Measure the high field close to the cathode in the hydrogen discharge from a study of the Stark effect in that region.
4. Observe the effect on the optical properties of the hydrogen plasma, of cooling to liquid nitrogen temperature.
5. Investigate the decay of the plasma by a spectroscopic study of the afterglow. Such an investigation is well suited to this type of plasma, as initial conditions can be accurately found.
6. Compare the mechanism and properties of the hydrogen plasma with those of helium<sup>1</sup>, and with those of other gases, for example, an electronegative gas such as oxygen.

#### Summary of Progress

The hydrogen brush cathode plasma has been investigated in a 4 cm diameter quartz tube, containing a brush cathode and ring anode placed a distance apart of 12 cm. The brush cathode used in the present study consists of a closely packed cylindrical arrangement of molybdenum wires. The wires do not touch each other, except where bunched together at one end. At the other end, the wires form a set of sharp planar points. The diameter of the brush is just less than that of the tube, and its length is 3 cm. Power was obtained from a 5000 V D.C. supply.

Maximum hydrogen purity was ensured by passing the gas through a palladium leak, and flowing it through the tube during investigation of the plasma. The main experimental difficulty encountered was the tendency of the discharge to strike to the edge of the brush cathode, as well as to the planar points. This was believed to be due to metal sputtered on the tube wall forming

a conducting path past the front of the cathode. The problem was solved by placing a 5 mm length of glass tubing around the front edge of the brush cathode; this broke the conducting path, as no metal sputtered onto the tube over the 5 mm length.

The pressure range from 0. to 3 mm Hg has been studied, and preliminary results indicate that the hydrogen plasma behaves rather similarly to that in helium<sup>1</sup>. Typically at a pressure of 1 mm and current of 30m A, a purple negative glow fills the entire tube, apart from a narrow cathode dark space (~ 3 mm), and bright pink cathode glow, which can be observed in the volume of the brush, as well as for a short distance (~ 1 mm) in front of the cathode. The boundary between the negative glow (plasma region) and the cathode dark space is sharp and flat. Current decrease moves the plasma boundary away from the cathode, decreases the light intensity from all regions, and reduces the overall plasma length. For all pressures below 1 mm, similar phenomena are observed, although in the 500 micron region, blue fluorescence of the tube wall dominates the plasma glow. At pressures of 1 mm and greater a pink anode glow exists at low currents; this disappears as the current rises above 10 m A. Above 1.5 mm the anode glow persists throughout the current region studied, 0 to 100 m A.

Data on the electric field in the region between the cathode and plasma boundary was compiled from Stark effect measurements. The  $\pi$  components of the  $H_{\beta}$  line gave the most easily observed splitting ( $\sim 0.5 \text{ \AA}^{\circ}$ ), both in the cathode glow and cathode dark space. Measurements showed that the total tube potential was concentrated between cathode and plasma boundary. No Stark effect was observed in the negative glow, the  $H_{\beta}$  line being very narrow here compared to the high field region. These results indicate that electrons accelerated by the field form a high energy beam, which generates a field-free negative glow, or plasma. The reason for the existence of such a large field is still not clear, although it may be due to the formation of a high density

positive ion space-charge region in front of the cathode. A higher density than that found using a normal cathode may result from the larger cathode surface area associated with the brush cathode.

Spectra of the plasma have been obtained in the ultraviolet and visible regions. It was hoped to measure charge-carrier concentrations and electron temperature by analysis of the Balmer series limit and the associated continuum<sup>2,3</sup>. This however, has so far proved impossible. The first few lines of the Balmer series can be clearly observed, but the presence of large numbers of molecular lines makes further analysis difficult. The highest order line of the Balmer series to have been resolved is H<sub>g</sub>. Furthermore, an investigation of plasma parameters using a Langmuir probe revealed a relatively low electron concentration of the order of  $10^{10} \text{ cm}^{-3}$ , while the electron temperature was about 8,000°K. Such a concentration does not allow analysis of the plasma using the series limit, as a positive ion concentration of the order of  $10^{12} \text{ cm}^{-3}$  is required before any effect on the limit can be observed. The problems existing are therefore those of low dissociation and ionisation in the plasma and attempts to overcome them will be made by going to higher tube currents, and by adding varying amounts of helium to the plasma.

Current voltage characteristics for the discharge were plotted at several pressures, and these are very similar to those obtained in helium<sup>1</sup>.

Two further quartz tubes have been designed. In these the cathodes are of tungsten, used to reduce sputtering. In one, the cathode is fitted using O-rings, to facilitate cleaning, and an opening at the anode end will allow probes or additional gases to be added. The second tube is sealed off to allow it to be cooled to liquid nitrogen temperature. Both tubes have been designed to allow them to be used for afterglow studies.

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## VELOCITY OF SOUND IN VAN DER WAALS CRYSTALS

S. L. Shapiro

Abstract

Preliminary experiments investigating Brillouin scattering in selected materials are in progress. The main goal is the detection of Brillouin scattering in the simple molecular crystals of  $N_2$ ,  $O_2$  and Argon in order to learn more about van der Waals' crystals. Although measurements on the elastic properties of polycrystalline argon have been carried out by the ultrasonic method, crystals grown by the modified Bridgman technique have never been analyzed for elastic constants.

Objective

The method to be tried for measuring the elastic constants is to use a He-Ne laser at 6328A to excite Brillouin scattering.

The object is to obtain information about the crystal structure by looking at the positions, intensities, and shapes of the Brillouin lines. The velocities of sound in the crystal may be obtained by an accurate measurement of the position of the Brillouin components, the intensities give a measure of the probability of photon-phonon interactions, and the half width of the line gives a measure of the lifetime of the phonon (attenuation coefficient).

A parameter which will be varied is the temperature, since the thermal waves (acoustic waves) are a function of T. In addition the crystals may be doped with impurities and the resulting intensities, positions and half-widths of the Brillouin lines measured.

Provisional Program

1. Irradiate liquids and solids to repeat other investigators' work.

2. Irradiate Ar, O<sub>2</sub> and N<sub>2</sub> crystals
3. Dope Argon with O<sub>2</sub> and irradiate in order to measure the attenuation of sound waves as a function of the partial pressure of oxygen and the temperature.

### Summary of Progress

Some experimental equipment has been assembled and preliminary experiments are underway to test the feasibility of the experiment. In initial experiments, liquids are being irradiated with a small He-Ne laser at 6328Å. The Brillouin shifts will be measured by using a Fabry-Perot interferometer. The velocities of sound in liquids are about the same as the velocity of sound in crystalline argon. Such a crystal is held together by very weak van der Waals' forces and hence the velocity of sound (~ 1700 m./sec) is rather small as compared to other solids. The Brillouin scattering formula applies. It is

$$\Delta\lambda = \lambda^2 \frac{nv}{c} \sin \varphi/2$$

n = index of refraction (for argon ~ 1.25)

c = speed of light

λ = wavelength of laser light

Δλ = wavelength shift of Brillouin line from laser lines

φ = angle of scattering

Thus far, no Brillouin scattering has been observed. The cause for this is not yet understood and efforts are being made to locate the difficulties. In addition a review of the published literature on Brillouin scattering is being undertaken.

## VII.

### FREE CARRIER MOBILITY IN SOLID AND LIQUID RARE GASES

H. D. Pruett

#### Abstract

Several additional pieces of experimental equipment have been added to the existing apparatus. Numerous experimental difficulties have been solved, and conductivity pulses have been observed in liquid and solid argon.

#### Objective

The objective of these investigations is to determine the nature of a few simple free-carrier interactions in rare gas liquids and solids.

#### Program

1. Develop a technique for growing crystalline rare gas solids between metal electrodes, suitable for measuring the free-carrier mobilities in such materials.
2. Compare positive and negative free-carrier mobilities in liquid and solid argon at temperatures near the triple point of argon ( $83^{\circ}\text{K}$ ).
3. Measure free-carrier mobilities in solid argon as a function of temperature and as a function of impurity density for various impurities.
4. Measure height of conductivity pulses in solid argon as a function of applied voltage and as a function of impurity content.
5. If possible, use results of these measurements as the basis of a theoretical model to explain simple electron interactions which predominate in van der Waals' solids.

#### Summary of Progress

Experimental investigations to determine the free carrier mobility in solid argon have continued through the period covered

by this report. At the beginning of this period, several attempts were made to use optical excitation as a means of generating free carriers in solid and liquid argon. The attempts were unsuccessful and optical excitation methods were discarded in favor of the original alpha-particle induced excitation method.

A temperature control system using liquid oxygen as a refrigerant has been completed and is presently in use. This evaporative cooling system permits easy and accurate control of temperature over the liquid oxygen pumping range. If still lower temperatures are desired, other liquids, such as hydrogen or neon, could be used as the refrigerant.

An automatic pressure regulator for use with the evaporative cooling system as also been completed. The regulator, which is connected in parallel with throttle valves between the refrigerant and the vacuum pump, will maintain a given pressure to within  $\pm 1$  mm Hg. This means that the temperature of the refrigerant can be controlled to within  $\pm 0.1^{\circ}\text{K}$  for most of the temperature interval of interest. Refinements on the regulator could improve the temperature control to plus or minus a few millidegrees, but such accurate temperature control is not needed for the present investigations.

In order to study conductivity pulses in liquified rare gases, a 10 KV power supply has been procured. Using electrode spacings of less than 1 mm, electric field strengths in excess of 100 KV cm can be obtained. When using such narrow electrode spacings, the capacitance of the electrodes introduces part of the output ripple of the power supply onto the desired signal. To eliminate this problem, a high voltage ripple filter was constructed having an attenuation factor of about 72 db for 120 cycle ripple. The ripple filter is also effective in eliminating some rather curious insulation breakdown pulses apparently caused by high energy cosmic rays.

An oil diffusion pump system has been constructed so that the cell where the rare gas crystals are grown can be evacuated

to a pressure of about  $1 \times 10^{-6}$  mm. This step was taken to insure a clean system prior to introduction of the ultra-pure gases used for growing crystals. In addition, an activated charcoal trap, operated at liquid oxygen temperature, has been added between the rare gas supply and the working cell. These two steps were taken in an attempt to reduce the oxygen impurity content as much as possible. Some related electron attachment studies<sup>1</sup> in liquid argon have shown how significantly oxygen as an impurity can reduce the magnitude of the expected conductivity pulses.

Conductivity pulses have now been observed in both liquid and solid argon. Electrical pick-up noise problems have prevented the taking of quantitative data. This troublesome problem has not yet been completely solved.

#### Future Plans

Plans for the immediate future are to begin taking quantitative data on free carrier mobility in rare gas solids and liquids as soon as an acceptable signal to noise ratio is obtained. Mobility data will be taken as a function of temperature and pulse height data will be recorded as a function of applied voltage.

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## VIII.

### A SPECTROSCOPIC STUDY OF THE CHARGE TRANSFER MECHANISMS IN BENZENE IODIDE

J. S. Margolis

#### Abstract

An attempt is just underway to investigate the visible and near ultraviolet spectrum of iodine-benzene complexes. Insofar as is possible the investigation will be made using single crystals or clear polycrystals of the solid material. The investigations will be made over a temperature range which extends from room temperature to liquid helium temperatures.

#### Objective

The objective of this study is to determine the nature of the interaction between the iodine molecule and benzene by the study of their spectra.

#### Program

1. Produce good single crystals of benzene and benzene iodide. These must be made on the order of 0.5 mm thick and in a container which will transmit the near ultraviolet light used in the experiments.
2. Build up a cold cell which will allow the spectra of the complex to be taken at liquid helium temperatures.

#### Summary of Progress

In the time that this investigation has been in progress it has been learned how to make good clear crystals of solid benzene. An apparatus has been built up for this purpose and a new crystal growing tube has been designed to grow crystals sufficiently thin for this study.

### Future Plans

The new crystal growing will be built and the spectra of crystals made in it will be taken with the Fastie-Ebert scanning monochromator.

IX.

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Milne, E. L., Steinberg, M. and Broida, H. P.  
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## 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) The Regents of the University of California Berkeley, California		2a. REPORT SECURITY CLASSIFICATION Object classification 250	
2b. GROUP			
3. REPORT TITLE "QUANTITATIVE STUDIES BY OPTICAL SPECTROSCOPY OF ENERGY EXCHANGE MECHANISMS IN SIMPLE GASES AND SOLIDS"			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Semi-annual Technical Report on period July 1, 1964 through December 31, 1964			
5. AUTHOR(S) (Last name, first name, initial) Broida, H. P., Principal Investigator Woolsey, G. A. Schofield, K.		Milne, E. L. Margolis, J. S. Dunn, J. L. Pruett, H. D. Shapiro, S. L.	
6. REPORT DATE 1 January 1965	7a. TOTAL NO. OF PAGES 30	7b. NO. OF REFS 14	
8a. CONTRACT OR GRANT NO. NONR 4222(01)	8a. ORIGINATOR'S REPORT NUMBER(S) Technical Report #2		
b. PROJECT NO. ARPA ORDER 125, Amend. #8	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
c.			
d.			
10. AVAILABILITY/LIMITATION NOTICES Limited number available on request			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U. S. Navy Regional Finance Office Eleventh Naval District 937 No. Harbor Drive San Diego 32, California	
13. ABSTRACT Emission studies have continued in fast flow systems of nitrogen energized in a microwave discharge. By changing parameters of pressure, temperature, and mixture, silicon tetrahalides added after the discharge have produced two electronic systems of SiN, and two separate, unidentified emitters in the green and in the orange spectral regions. Addition of CO <sub>2</sub> , N <sub>2</sub> O and CO has shown near infra-red emission of these molecules, caused by transfer of vibrational energy from the ground electronic state of molecular nitrogen. To further the understanding of the N <sub>2</sub> <sup>+</sup> emission observed in some afterglows, a detailed perturbation calculation for the v = 1 level of the B <sup>2</sup> Σ state and the v = 11 level of the A <sup>2</sup> Π has been undertaken. A new set of studies in a well-behaved plasma produced by means of a brush cathode has been undertaken. Spectroscopic, electron probe, and voltage-current measurements are being made in hydrogen and in hydrogen-helium mixtures at pressures near 1 mm Hg. The condensed phase studies of molecular solids has not had any significant results. A review article on "Flame Kinetic Studies" is being prepared for publication in an Academic Press, Inc. series on "Methods in Experimental Physics", Volume VIII entitled "Atomic Physics".			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Charge-transfer complexes Optical Spectroscopy Energy Exchange Vibraluminescence Molecular crystals Plasma						

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