EMISSION SPECTRA OF SIMPLE HYDROCARBONS EXCITED IN A RADIO-FREQUENCY PLASMA

by

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CHAPTER I

INTRODUCTION

History and Purpose

In 1802, Wallaston observed the so-called Swan spectrum by looking at the flame of a candle through a prism. During the 1800's the species responsible for this spectrum was sought. With the advent of quantum mechanics in the early part of the twentieth century, this species was identified as C_2 and the spectrum was completely deciphered as to energy states and molecular configurations of the species, and indeed other bands were predicted and later found.

Interest in the system came about due to the role played by the C_2 molecule in combustion and related phenomena. However, a satisfactory mechanism of combustion has not yet been found. In fact, the method of formation and excitation of the C_2 radical is still unknown. It was with this in mind, that a proposal was made to study further this C_2 system and it's related systems to acquire more information as to their mechanism of formation and excitation.

The investigation was carried out using a relatively new method of excitation on several hydrocarbons - excitation with a radio-frequency plasma.

A search of the literature revealed no previous work on molecular emission spectra using the plasma for excitation.

Beginning with an elementary discussion of the theory of atomic and molecular spectra and continuing with a discussion of the plasma state and other methods of excitation, a description of the apparatus used as well as the procedure followed in obtaining the results is given. The results of the analysis of the spectra will be introduced in tabular form. Generally, these results will be discussed in terms of the various methods of excitation.

CHAPTER II

THEORY

Atomic and Molecular Spectra (1)

In discussing atomic and molecular spectra, one must talk in terms of energy. It is known that energy can be neither created nor destroyed. For example, a pan of gasoline has no kinetic energy. However, when heat or fire is brought near, the gasoline burns in air and kinetic energy is produced. Similarly, illuminating gas, when brought near fire, will burn and release energy. Some of this energy is released in the form of light, and if the same conditions prevail, the nature of this light will be the same. Although heat is also being emitted, this is somewhat difficult to study as compared to light emission which is easily photographed.

What is happening in this emission process? We believe, from Classical and Quantum theory, that atoms and molecules possess discreet energy levels. The electrons orbiting the nucleus or nuclei, are in certain levels, the so-called ground state. It is possible to excite one or more of these electrons to an energy level farther removed from the nucleus, the so-called excited state. The subsequent return of these electrons to the ground state emits radiation in the form of heat and light. This radiation obeys the equation $\Delta E = E_2 - E_1 = h\nu$, where ΔE is the change in energy, E_2 being the energy of the excited state and E_1 the energy of the ground state. In this equation, h is a constant known as Planck's constant and ν is the frequency of the radiation.

Another result of quantum mechanics is that this particular type of emission takes place in quanta at definite wavelengths. These energy levels are at definite distances from the nucleus and the electron may return to the ground state or any other lower level, but only to these discrete levels. Then by continued processes or a series of processes, the electron may return to its ground state.

There are certain allowed and unallowed jumps or transitions, all governed and summed up by selection rules which are a result of the quantum numbers of the electron taking on various values.

In looking at an atomic spectrum, the most noticeable characteristic is the grouping of the atomic lines into series. The frequency of a particular line, ν_i, is given by $\nu_i = \nu_\infty - R/i+C$, where ν_∞ is the frequency of the series limit, R and C are constants for the particular series, and i is an integer taking on values of one to infinity. Atoms are thus characterized by line spectra.

Let us take a simple example to show the results of this theory. The hydrogen atom is the simplest atom, but will serve to point out the theory for more complicated atoms.

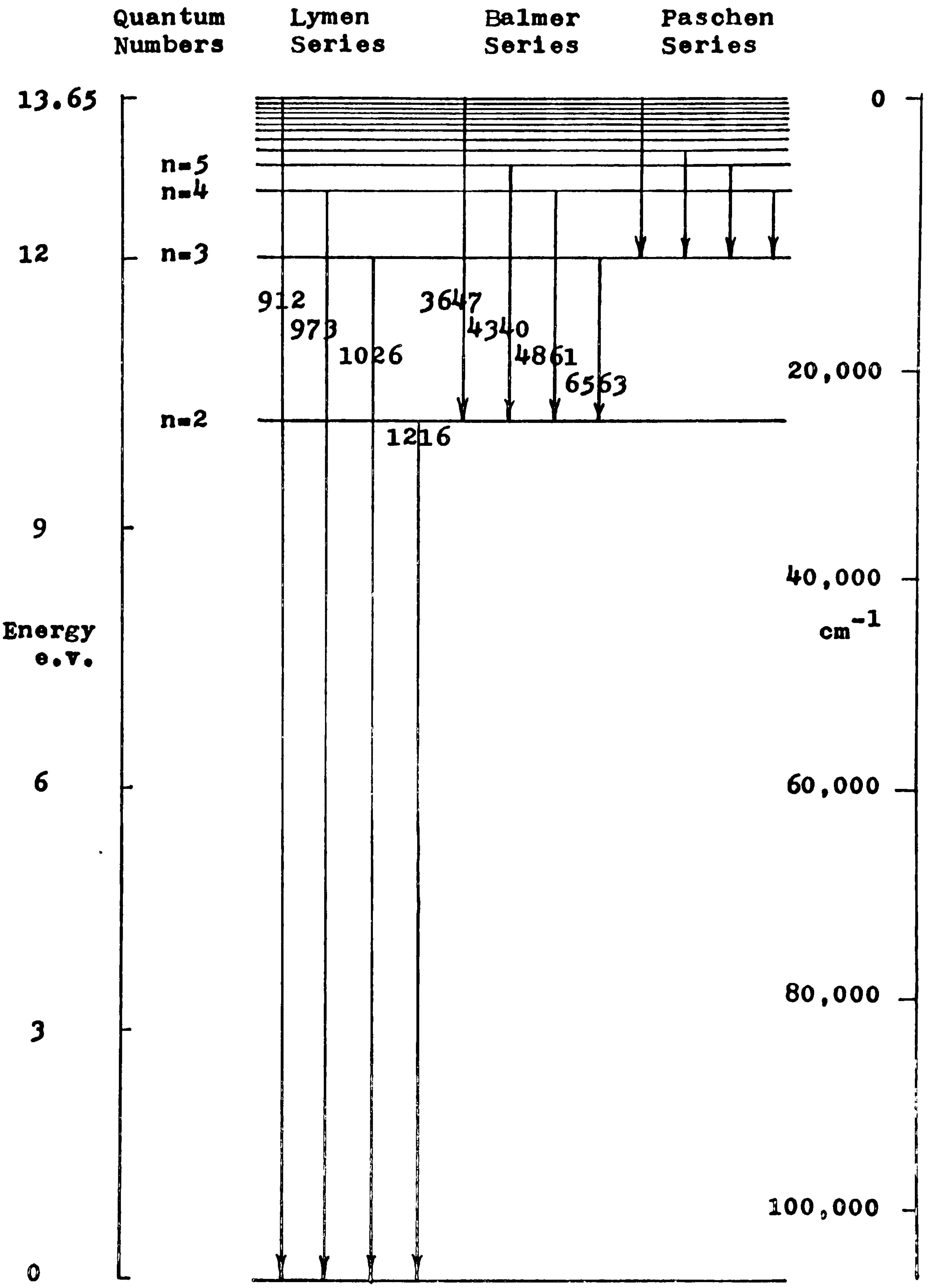
The frequencies for emission of radiation for the hydrogen atom are given by $\nu_{ij} = R_h\ (1/i - 1/j)$, where i is smaller than j. Thus, j represents the excited state and i the ground state and ν_{ij} the frequency of emission for an electronic transition from the jth to the ith level. A series of lines which occur when i = 1 and j varies from 2 to infinity is called the Lyman series. For i = 2 and j = 3 to infinity, the Balmer series is seen. This continues through the Pashen and Pfund series. This can be seen better in a diagram (Figure 1) of the energy levels of the hydrogen atom. Here, the upper part of the diagram represents the higher energy. We see also the energy levels, as well as the different transitions grouped into series. A line between two levels represents a transition from the higher to the lower level with the corresponding emission of radiation.

In the same manner, atoms with more than one electron can become excited and various electrons occupy different energy levels. The return of these electrons to the various levels becomes more complicated but produces related spectra.

If enough energy is put into this atom, it is possible to raise an electron to an energy level far enough removed from the nucleus so that this electron is no longer associated with the atom and ionization has occured.

Thus, a line spectrum occurs when an electron, which has become excited, returns to a lower energy level with the simultaneous emission of radiation.

Just as an atomic spectrum is due to the excitation of an electron in an atom, a molecular spectrum is due to the excitation of an electron in a molecule. However,



Grotrian Diagram for Atomic Hydrogen

Figure 1

atomic radiations are characterized by line spectra while molecular radiations are characterized by band spectra.

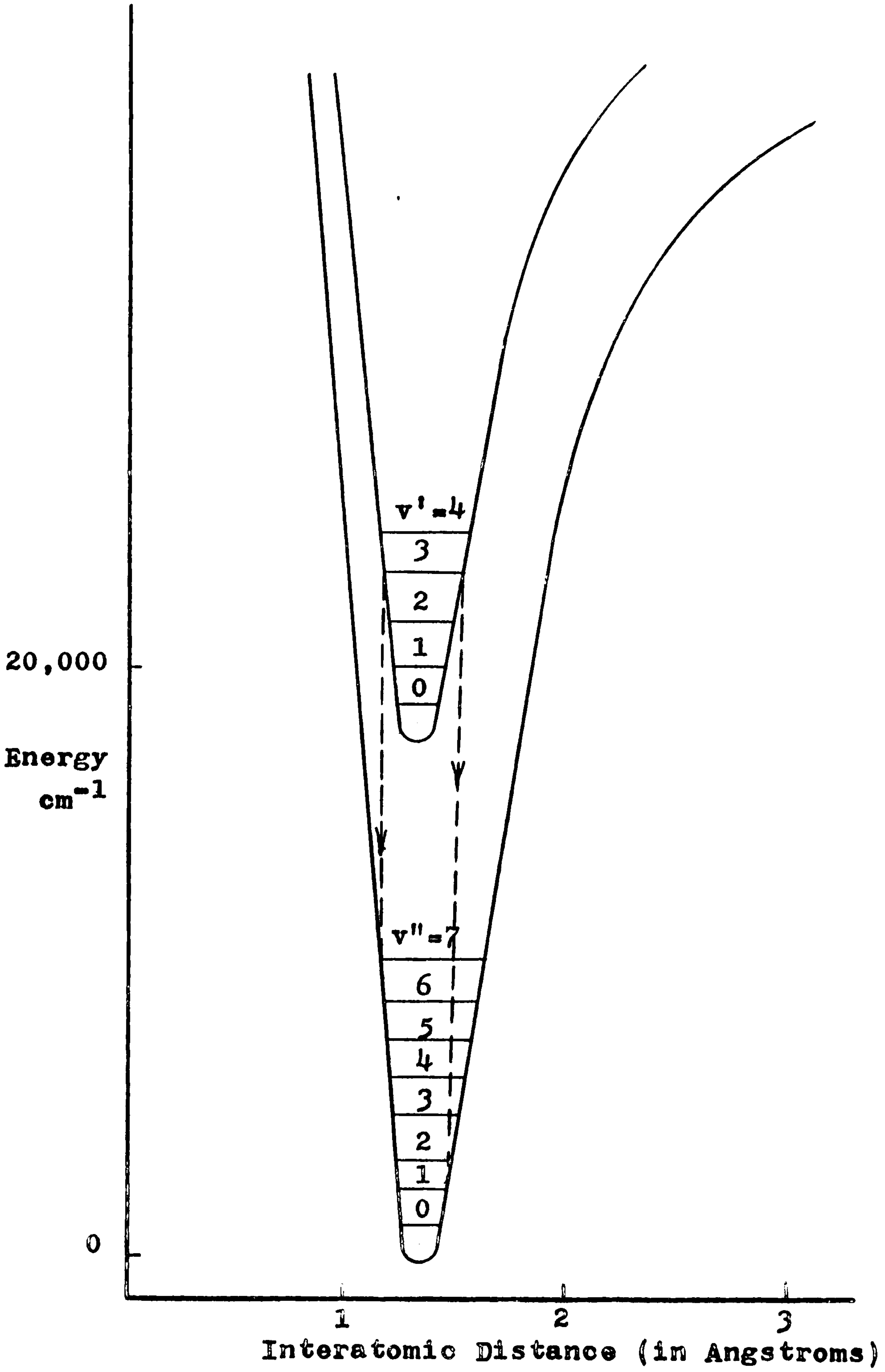
Since a molecule is composed of two or more atoms, molecular spectra are much more complicated than atomic spectra. A fundamental equation relating the various types of energy in a molecule is that the total energy for a given state of excitation, $E_t = E_{el} + E_{vib} + E_{rot} + E_{tr}$, which is the sum of the electronic, vibrational, rotational, and translational energies. As we have seen, a transition is represented by a change in energy, ΔE, so that the total energy change in a molecular transition is represented by the equation $\Delta E_t = \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot} + \Delta E_{tr}$. The translational energy change is insignificant when compared to the others and thus will not be discussed further. But let us look at these other three types of energy.

The rotational energy is related to the angular velocity with which the molecule rotates. This rotational energy is entirely kinetic and is dependent on the moment of inertia of the molecule. The quantum mechanical treatment provides certain rotational selection rules which permit only certain angular velocities and thus, the molecule has distinct rotational energy levels. Since the rotational energy is dependent on the moments of inertia of the molecule, the geometric shape of this molecule greatly influences this energy.

A molecule containing N atoms has 3N kinds of motion. Three of these motions are translational, three are rotational about the three axis of rotation (2 for a linear molecule), and the remaining $3N-6$ ($3N-5$ for linear) motions are vibrational. There is a fundamental frequency associated with each fundamental vibrational motion called the vibration frequency. Also, there is a separate quantum number for each vibration giving again distinct energies of vibration. Thus there is a group of energy levels corresponding to different quantum states which sum together to give a single frequency. These levels are characterized for a theoretical molecule, as being equally spaced and having an energy for the lowest level of $\frac{1}{2}h\nu$.

We have seen that atomic emission spectra consist of the excitation of an electron to a higher energy level and the return of that electron to some lower level accompanied by the emission of radiation. Similarly, electrons in molecules may be excited and return and give off radiation. Again, this excitation must occur to a definite higher energy level as stated by the quantum numbers and the selection rules. These electronic energy levels show a strong dependence upon the attractive force of the electrons within the molecule, for it is obvious that if enough energy is put into the molecule, it would break apart into its individual groups or atoms.

This is illustrated on a potential energy diagram of C_2 (Figure 2) which shows the relations among these energies. (2) In the diagram, the energies of two electronic energy levels are represented by the two curves. Several vibrational levels, which are discrete, are also shown.



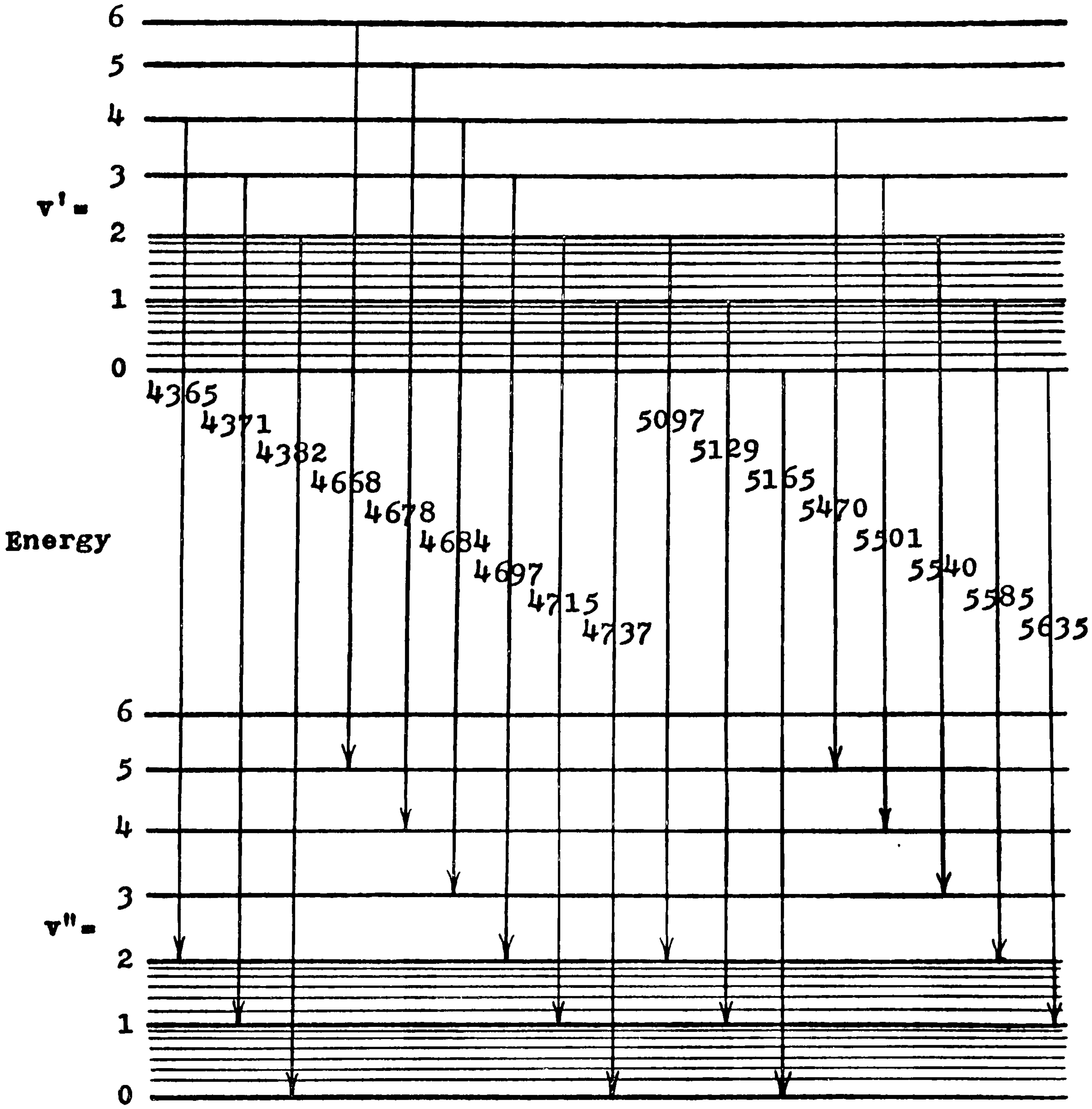
Potential Energy Curve for C_2 Swan System
Figure 2

The dotted vertical lines represent transitions which appear as bandheads in the emission spectrum. Figure 3 is the energy diagram for the C_2 Swan system. (1) Several observed transitions are shown with wavelengths given. The fine lines represent rotational levels of which only a few are shown, while the dark lines represent vibration levels.

In order of magnitude, an electronic transition ($\Delta n=1$) requires much more energy than a vibration transition ($\Delta v=1$) which requires again, much more energy than a rotation transition ($\Delta r=1$) and therefore, an electronic transition is necessarily accompanied by the other two, while a vibration transition may be accompanied only by a rotation transition.

It is known that the energy of the electronic change determines the general location or position of the spectrum on the wavelength or energy scale, while the vibrational change determines the spacing of the individual bands and the rotation change determines the fine structure of each of the vibrational bands.

In summing up, we see that an electron in an atom may be excited by various means to a higher energy level and the return of this electron to some lower level causes emission of radiation, characteristic of this particular energy change in the atom. Similarly, electrons in a molecule may be excited and emit radiation, but this emission will be more complicated due to the various vibrations and rotations which the molecule may possess. A single



Energy Diagram of C_2 Swan System

Figure 4

radiation is characteristic of a particular transition in a single species.

Plasma Theory

A plasma may be defined as a mass of ionized gas in which the concentrations of electrons and positive ions are in equilibrium. The greater mobility of the electrons, as compared to the heavier positive ions, causes the electrons to move outward and produce a negative sheath. If the total volume of positive ions and electrons is large with respect to the negative sheath, a plasma forms. (3)

A plasma is observed when a gas or vapor, across which a voltage gradient exists, becomes electrically conducting by transition to the plasma state. Usually these plasmas are confined to a specific volume. In this thesis, a plasma will refer to that type which is not confined and has the appearance of a moving or streaming plasma.

Flame Theory (4)

In flames, excitation occurs mainly as a result of collisions between molecules and atoms. One characteristic of the band systems obtained with flames is that the systems arise from the lower lying energy levels, and the upper energy level rarely exceeds five electron volts. These bands are due to molecules which are electrically neutral. Flames, of course, require a fuel as well as an oxidizer. In a common case, this fuel is a hydrocarbon and the oxidizer is oxygen or air.

The hydrocarbon flames readily produce the C_2 Swan bands, the CH bands, and the OH bands. The transitions which cause these bands are of low enough energy so as to be produced by a flame. It is interesting to note that the NH system and the CN system occur only in flames which contain nitrogen in the combined form, either in the fuel or the oxidizer. The CO Angstrom and Third Positive bands, which require more than ten electron volts for excitation, are absent in normal flames.

Other Methods of Excitation (4)

There are, of course, other methods of excitation and these methods will now be discussed.

Arcs, in general, develop much higher temperatures than flames and are able to excite atoms to a much higher energy state and even to produce ionization. Due to this higher temperature, a molecule is excited to a higher energy and there are more paths for the electron in the molecule to return to the ground state. Thus, many more band systems in various regions of the spectrum may occur. Arcs are usually the result of the passage of a high current at low voltage between two electrodes. An arc between carbon electrodes in air has enough energy to activate the nitrogen in the air. The nitrogen then behaves as nitrogen in the combining form and by reaction with the carbon from the electrodes, the CN bands are produced. Generally, the arc is not used in the study of the emission bands of hydrocarbons because this high energy completely breaks up the hydrocarbon and other molecules.

The spark is also associated with very high energies and produces mainly, atomic spectra. The spark is characterized by high voltage at low current through two electrodes. For similar reasons, the spark is seldom used in the study of emission spectra of hydrocarbons.

A third type of excitation is the discharge tube. These tubes operate from spark coils or transformers supplying high voltage and low current. A convenient form for spectrographic use is the so-called Geissler tube which is a quartz tube containing an enlarged portion at each end of a connecting, constricted tube. The electrodes are contained in the enlarged portions and the concentrated light of the discharge is viewed in the constricted tube. These tubes may be obtained unfilled so that the tube can be evacuated to a low pressure and the gas under investigation may be added. These tubes must be operated at low pressure to allow the ready flow of electrons from one electrode to the other.

The more luminous regions of the normal discharge are the positive column and the negative glow. The spectra obtained in the positive column are usually those of uncharged atoms and molecules, but a higher energy is available and thus, in the proper medium, the CO Angstrom bands appear in this positive column.

The negative glow, on the other hand, gives largely the spectra of positively charged ions. A modification of this negative glow is obtained in the hollow cathode discharge tube, which results in a more brilliant source.

An interesting method of excitation is the electrodeless high frequency discharge. In this case, a high frequency tuned oscillator is used to maintain the discharge. The energy of the oscillator is transferred to the gas contained in the tube by several methods. The oscillating circuit may be connected to external electrodes consisting of foil wrapped around the outside of the tube or to a wire coiled around the tube in the form of an inductance coil. With this arrangement, the gas in the tube at low pressure is caused to glow and emit the radiation characteristic of the species present. High frequency discharges are advantageous in that the contamination from the electrodes is avoided.

CHAPTER III

APPARATUS

Plasma Generator

There are several different methods of producing a plasma. These methods are briefly discussed with more emphasis on the method used in this research.

The constricted arc is a well developed device for producing plasma. (5) This generator consists of a high current electric arc contained within a small tube through which a gas is blown with the result that the plasma is jetted through a nozzle. This device uses a cooling system around the nozzle thus preventing any vaporization and corrosion of the electrodes.

Another type of generator is the microwave generator. Microwave coupling through a resonance cavity gives standing waves whose pattern depends on the size and shape of the cavity. (5) To obtain the microwave discharge, a magnetron tube is often employed with the proper microwave circuitry.

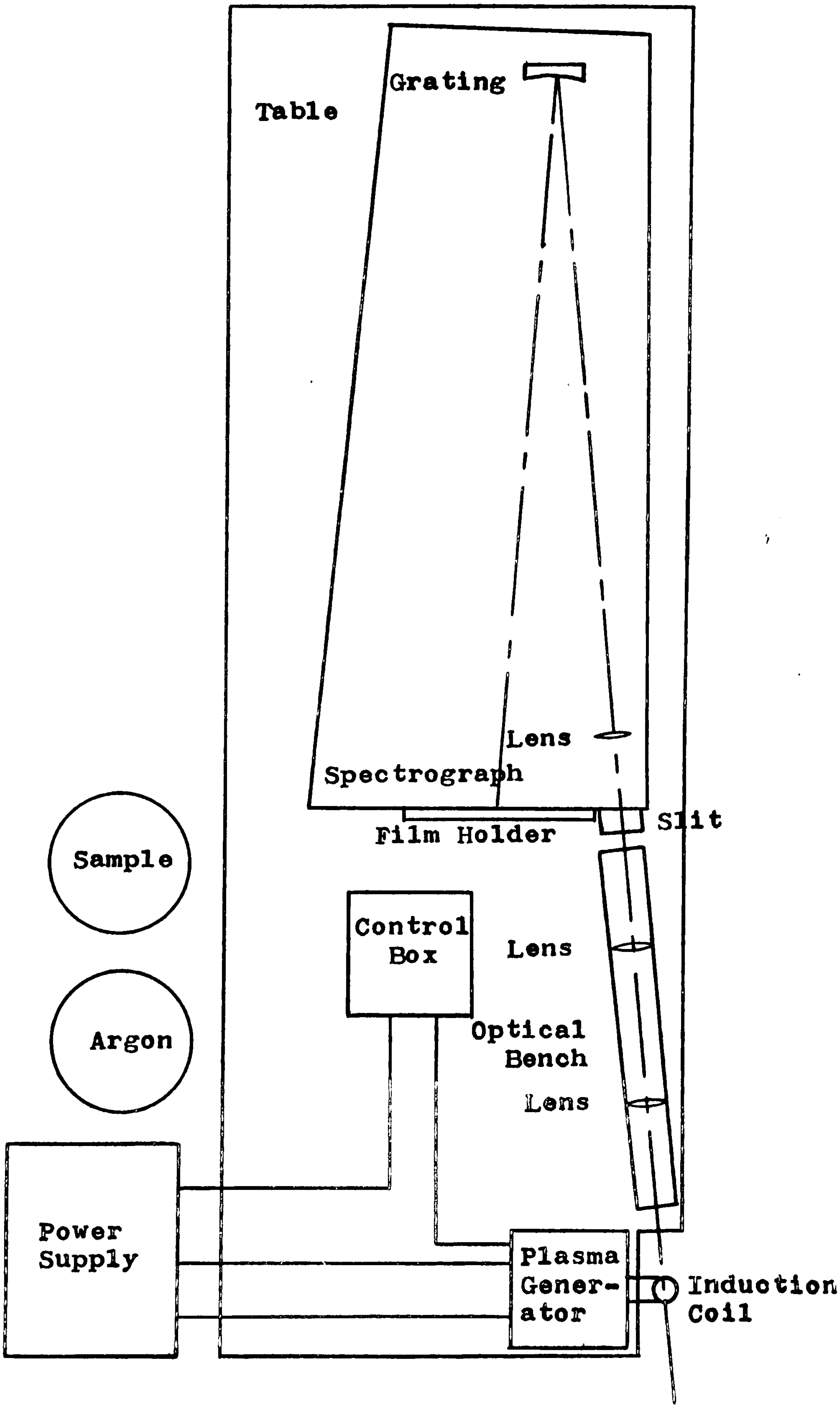
In this laboratory the induction heated plasma torch was used for exciting the hydrocarbons. (3) This type of plasma torch uses a radio-frequency field to maintain a thermal plasma without the consumption of electrodes. The energy of the high frequency electromagnetic field is transferred to the gas by interactions with the ionized gaseous molecules, atoms, and electrons and thus maintains a high degree of dissociation and excitation. The return of molecules from high states of excitation as well as allowed recombinations of separated groups, results in absorbed energy being given off in the form of heat and light. The field producing this energy is from a 27 megacycle transmitter. The schematic diagram of this transmitter is rather simple. The generator consists of a conventional tuned plate, untuned grid oscillator. In this laboratory, a 1900 volts DC power supply was employed giving about 250 watts output of the generator. A slight modification of the generator of Roddy and Green (3) was made in order to completely eliminate electrode contamination. The working coil used in this laboratory consisted of seven turns of ¼ inch copper wire on a mean diameter of approximately 1¼ inches with an overall length of 4¼ inches. With this arrangement, the plasma was easily formed within the tube inside the working coil, and extended several inches below the coil so that the spectrum was easily photographed.

For a more complete description of the generator used see Reference (6).

Spectrograph and External Optics

The plasma generator with the induction coil, in which the plasma was produced, was set up at one end of an optical bench. Two glass lenses were positioned on the optical bench so as to focus the greatest amount of radiation on the slit of a spectrograph. Being of glass, these lenses allowed ultraviolet light as low as 3300 A to pass through. In order to distinguish between overlapping orders on the film, an ultraviolet absorbing filter which absorbed all radiation below 4200 A , was sometimes placed between the second lens and the slit.

The spectrograph employed in this research was a 1.5 meter Bausch and Lomb grating spectrograph. The slit assembly consisted of several pieces, one being a removable slit holder. On the slit holder there were three slit widths of 10μ , 30μ , and 60μ , ruled in aluminum on a quartz plate. A Hartman diaphragm with seven holes was furnished with the slit assembly; however, a new diaphragm with four rectangular holes was constructed in order to facilitate this particular study. A hand operated shutter was present on the slit assembly. The internal optical system consisted of a stigmatizing cylindrical quartz lens and a concave grating which has 450 lines per millimeter and a spectral range of 3700 A to 7400 A in the first order and 1850 A to 3700 A in the second order. A film holder was fixed adjacent to the slit and secured to the spectrograph with ear fasteners. The film holder assembly required standard 35 millimeter film. The type used in this investigation was Kodak Type 103-F which has a high spectral sensitivity from 2300 A to 6700 A. A block diagram of the generator, optical bench, lens system, and spectrograph appears in Figure 4.



Block Diagram of Apparatus

Figure 4

Gases

In order to stabilize the plasma with the low powered generator used, a carrier gas was necessary. Argon was used in all cases at atmospheric pressure because of its low heat capacity at ionizing temperatures and because of its poor thermal conductivity. (7) The argon used in this study was that commercially available from standard gas cylinders.

Since this work was of a general investigative nature at the start, several hydrocarbons were introduced into the plasma in an effort to choose a sample and establish conditions under which to run a more detailed study. Four samples were finally chosen; propane, n-butane, carbon tetrachloride, and chloroform. The propane is that which is bottled for home use in various torches and stoves. The n-butane was extra pure, spectroscopic grade material. In order to ascertain the purity of these gases, mass spectrographic analyses were run. The data was compiled and it was shown that the argon was very pure, containing approximately 0.31 percent air or approximately 0.25 percent nitrogen and 0.06 percent oxygen. The n-butane was of high purity since it contained no detectable impurities as recorded on the mass spectrograph. The propane was surprisingly pure. The propane used, which was bottled by Otto Bernz Company, Incorporated, Rochester, New York, showed no appreciable nitrogen and approximately 1 per cent propene.

The two liquid samples, chloroform and carbon tetrachloride, were laboratory reagent grade and no determinations were performed to show their purity. It was found that the direct introduction of liquid samples tended to extinguish the plasma and therefore, all liquid samples were vaporized before introduction. The sample was vaporized in an externally heated glass bulb and in all cases, very small quantities of sample were introduced.

Sample Handling Techniques

A system of Pyrex glass tubing, in which to mix the sample with argon, was set up and led through the working coil of the plasma generator. Several ground glass stopcocks were put into this tubing system to facilitate the introduction of small samples under controlled conditions.

A system was set up so that these samples could be run at low pressures. A suction flask was attached to the tube on the other side of the working coil. This flask was then attached to several large stainless steel tanks which served as expansion chambers. A manometer was hooked into the vacuum line which was also attached to a large mechanical vacuum pump. Thus with very little effort, one was able to control the system from atmospheric pressure down to low pressure (10 to 20 mm Hg).

CHAPTER IV

EXPERIMENTAL PROCEDURE

It was desired to obtain the spectra of several hydrocarbons at both atmospheric and low pressure using the plasma for excitation. Initially, the spectra at atmospheric pressure were obtained. First, the external optical system and the excitation source were set up so that the radiation would fall on the film. A small electric light was held at a point in space where the plasma would be produced. The light from this small bulb was then allowed to fall on the grating and by viewing toward the grating at the plane where the film would subsequently be placed, it was a simple matter to adjust the external lenses and the position of the generator so that the maximum amount of radiation would fall on the grating. The light bulb was then removed and the system prepared for the run.

The argon and the gas sample were then connected to the glass tubing so that they would mix and travel in the tube through the induction coil. The spectrograph shutter was closed and the film holder containing the film was fastened to the spectrograph. The slit was then inserted until the proper slit width was in line with the optical system. The 60μ slit width was used throughout this study.

Various switches, located at a central control box, were turned on in proper sequence so that the power supply and generator were operating at low voltage. After several minutes for these components to warm up, a switch was thrown to place the generator on full power.

Next, the pressure regulator and flow valve on the argon tank were adjusted so that there was a flow of argon through the tube. In this investigation, a flow rate of from six to eleven liters per minute at twenty pounds of pressure was used.

The plasma was then started by inserting a carbon rod or copper wire inside the Pyrex tube in the induction coil. This rod or wire is heated inductively within the radio-frequency field. This in turn, heated the argon in the tube conductively and lowered its breakdown potential sufficiently for the plasma to be formed. The rod or wire is then slowly withdrawn from the tube. The plasma is stabilized by the spiral flow of the argon down the walls of the tube. (7) This argon plasma was allowed to run for several minutes during which the external optical system was again checked, the argon flow rate adjusted to the satisfactory value, and the dark slide in front of the film withdrawn so that all was ready for photographing the spectrum.

The valve on the tank containing the sample gas was opened and the stopcock in the gas handling system was adjusted so that only a very minute flow of sample gas was entering the plasma. This could be seen easily since the plasma changed color from the light purple of the argon plasma to the brilliant green of the plasma with argon plus sample. This plasma was allowed to stabilize for several minutes before the spectrum was actually photographed.

In all cases the spectrum was exposed for five minutes at atmospheric pressure. This was accurately timed with a small timer. The shutter was then closed, the ultraviolet filter inserted between the slit and lens, the Hartman diaphragm moved to the next position, and the spectrum again taken.

All valves and switches were then turned off and the vacuum system previously described was hooked up. The pumps were turned on and the system was pumped out for at least thirty minutes prior to taking the low pressure spectrum.

Argon was not necessary to maintain the low pressure plasma; hence the tube supplying argon was closed off.

During this waiting period, the ultraviolet filter was removed and the Hartman diaphragm was adjusted to the next slot. Then the generator was again turned on. A Tesla coil, whose two leads were connected to electrodes within the tube on either side of the induction coil, was used to start the plasma at low pressure. These leads were then removed and the sample gas was allowed to enter the tube. Again, the shutter was opened and the spectrum was photographed. The time of exposure for low pressure work was fifteen minutes due to the decreased intensity of the plasma. Two spectra were taken, one with the filter and one without.

The spectrum of the vaporized liquid samples was photographed in a similar manner, the only difference being in the method of introduction of the sample into the plasma. As was mentioned, the sample was vaporized by controlled heating at atmospheric pressure. The stopcocks were then adjusted to allow the sample to mix with the argon carrier gas and thus be introduced into the plasma. At low pressure, heating was unnecessary due to the relatively high vapor pressure of the liquids and it again was possible to introduce a small sample by opening a stopcock.

The exposed film was developed in Kodak D-19 developer for five minutes, washed in water, and fixed in Kodak F-5 fixer for twenty minutes. This was followed by a thorough wash in water and finally air drying. This developing procedure was carried out at room temperature.

Meanwhile, a small paper envelope was prepared upon which was affixed a code number and pertinent information concerning the spectrum. The film, subsequently, was marked with an identical code number and always kept in the envelope when not being used.

Several techniques were employed in the identification of the bands and lines of the spectrum. A standard iron spectrum was included on the initial spectrum. It soon became evident that the C_2 Swan system was present in each spectrum so the iron spectrum was discontinued and the C_2 Swan system, whose bands are easily identified, was used as the standard.

The spectrum was inserted into the film holder of a Bausch and Lomb densitometer to which a millimeter rule had been affixed. Since the spectrograph has a linear dispersion, it was possible to insert the scale reading and wavelength of a known band into a desk calculator, into which the dispersion on the film had already been placed, and by moving to an unknown band and inserting this scale reading into the calculator, the wavelength of this new band was obtained directly.

By a consideration of the sample gas and the possible species which could emit radiation, it was possible to identify many of the bands. This process was accomplished with the aid of several books giving complete wavelength tables for molecular bands. (4) (8) Atomic lines were identified with the help of another book. (9)

Thus, it was possible to obtain one well-marked spectrum. A comparison of this one with the subsequent spectra in a modified 35 mm projector made for fast and easy identification of most of the lines and bands.

Finally, to facilitate the identity of all lines and bands, the spectrum was enlarged and printed using standard photographic procedures. From a spectrum on a film 35 mm wide by 10 inches long was obtained the printed spectrum on paper 6 inches wide by 7 feet long. By comparing this printed, well-marked spectrum with another printed spectrum, it was possible to identify all lines and bands of the new spectrum.

CHAPTER V

RESULTS

Using the preceding procedure, many spectra were obtained for a variety of originating molecules and under several different conditions. Samples were then chosen and spectra obtained under controlled conditions. Data gathered from the analysis of these spectra, appear on the next several pages in tabular form.

Since the propane and n-butane spectra were identical except for intensity of the bands, only the analysis of the propane spectrum will be given. The chloroform and carbon tetrachloride spectra were also quite similar, the only exception being the absence of NH bands and CH bands in the spectra produced by carbon tetrachloride. There was also some variation in intensity and since the carbon tetrachloride spectrum, generally, was more intense, it is the one which will be reported. No intensity values were measured in this investigation since the main interest concerned the species which were present.

Table I gives the analysis of the two samples reported. In the first column, the species responsible for the radiation is given and this is given only once when two or more bands appear consecutively in the table. In this column the symbols in parenthesis, S, v, A, and P represent the Swan system of C_2, the violet system of CN, the Angstrom system of CO, and the Second Positive system of N_2, respectively.

The second column is the wavelength of this species as given in the references. (4) (8) The unit of measure for wavelength is the angstrom (A), which is 1 x 10^{-8} centimeters in magnitude. Following the usual notation for emission spectroscopy, the wavelength represents the radiation due to a transition from a higher to a lower energy level.

The rest of the table consists of four columns, where the first two columns are for spectra recorded at atmospheric pressure and the last two columns are for those spectra obtained at low pressure. As subheadings, the two samples propane and carbon tetrachloride appear so that an x in any particular column means that this species was found at the noted pressure with the particular sample.

Table II gives the atomic lines observed in the spectra. Generally, the same atomic lines were observed for all samples with the exception that the hydrogen lines had decreased intensity for the halogen containing hydrocarbons. The only atomic lines detected were those due to hydrogen and argon. This table is divided into two columns, the first column giving the atom responsible for the emission and the second column giving the wavelength as listed in the reference book for atomic lines. (9) It should be noted that only the more prominent argon lines are listed.

Examination of these tables reveals that when propane was the sample hydrocarbon, the following systems were observed at atmospheric pressure; C_2 Swan, CH, CN violet, and

TABLE I

ANALYSIS OF PROPANE AND CARBON TETRACHLORIDE SPECTRA BY PLASMA EXCITATION

Species	Wavelength (A)	Atmospheric Pressure		Low Pressure	
		C_3H_8	CCl_4	C_3H_8	CCl_4
NH	3360	x	x		
	3370	x	x		
N_2 (P)	3371.3			x	x
	3536.7			x	x
	3576.9			x	x
CN (v)	3583.9	x	x	x	x
	3585.9	x	x	x	x
	3590.4	x	x	x	x
N_2 (P)	3671.9				x
	3710.5			x	x
	3755.4			x	x
	3804.9			x	x
CN (v)	3850.9	x	x	x	x
	3854.7	x	x	x	x
	3861.9	x	x	x	x
	3871.4	x	x	x	x
	3883.4	x	x	x	x
CH	3889.0	x			
N_2 (P)	3894.6			x	x
	3943.6			x	x
	3998.4			x	x
	4059.4			x	x

TABLE I (continued)

Species	Wavelength (A)	Atmospheric Pressure		Low Pressure	
		C_3H_8	CCl_4	C_3H_8	CCl_4
N_2 (P)	4094.8			x	x
	4141.8			x	x
CN (v)	4152.4	x	x	x	x
	4158.1	x	x	x	x
	4167.8	x	x	x	x
	4181.0	x	x	x	x
	4197.2	x	x	x	x
	4216.0	x	x	x	x
N_2 (P)	4269.7			x	x
CH	4312.5	x			
N_2 (P)	4343.6			x	x
	4355.0			x	x
	4416.7			x	x
	4490.2			x	x
CN (v)	4502.2	x	x	x	x
CO (A)	4510.9			x	x
CN (v)	4514.8	x	x	x	x
	4531.9	x	x	x	x
	4553.1	x	x	x	x
	4578.0	x	x	x	x
	4606.1	x	x	x	x
C_2 (S)	4678.6	x	x		
	4684.8	x	x		
	4697.6	x	x		
	4715.2	x	x		

TABLE I (continued)

Species	Wavelength (A)	Atmospheric Pressure		Low Pressure	
		C_3H_8	CCl_4	C_3H_8	CCl_4
C_2 (S)	4737.1	x	x		
CO (A)	4835.3			x	x
C_2 (S)	5097.7	x			
	5129.3	x	x		
	5165.2	x	x		
CO (A)	5198.2			x	x
C_2 (S)	5470.3	x			
	5501.9	x			
	5540.7	x			
	5585.5	x	x		
CO (A)	5610.2			x	x
C_2 (S)	5635.5	x	x		
	5923.4	x	x		
	5958.7	x	x		
	6004.9	x	x		
	6059.7	x	x		
CO (A)	6079.9			x	x
C_2 (S)	6122.1	x			
	6191.2	x			
CO (A)	6620.3			x	x

TABLE II

ATOMIC LINES

Species	Wavelength (A)
Hydrogen	6562.8
	4861.3
Argon	7067.2
	6965.4
	6871.3
	6752.8
	6416.3
	6059.3
	5650.7
	5495.9
	5162.3
	4510.7
	4333.6
	4300.1
	4272.2
	4266.3
	4259.4
	4200.7
	4198.3
	4181.9
	4164.2
	4158.6
	4044.4
	3948.9
	3947.5

NH. With the same sample, at low pressure the following systems were observed; N_2 Second Positive, CN violet, and CO Angstrom.

It must be noted that the conspicuous absence of the OH bands was due to possible absorption of the radiation by the Pyrex tube which contained the plasma or to the glass lenses used in the external optical system. These components did not transmit the radiation of 3064 A which is the head of the most intense OH band.

The C_2 Swan system has been thoroughly investigated for many years by several well known investigators but its mechanism of formation and excitation is still open to question. These bands are of very frequent occurance in hydrocarbon flames as well as in vacuum tube discharges containing hydrocarbon vapors. (4) This C_2 Swan system appeared with very high intensity in the plasma excitation at atmospheric pressure but was completely absent at low pressure. This indicates that the plasma excitation of C_2 is pressure dependent. The C_2 emission at atmospheric pressure was as intense as the CN violet emission and these two systems were the most intense on each spectra.

The two known systems of bands due to CN are the cyanogen red and violet systems. (4) They are both easily excited and occur in flames of cyanogen, in the carbon arc in air, in discharges containing nitrogen and carbon compounds, and generally, when hydrocarbons are excited in the presence of active nitrogen. It requires about 9.5 electron volts to activate the nitrogen molecule so that in the presence of hydrocarbons, the CN bands are produced. This amount of energy is not available in most flames so that hydrocarbon flames in air do not give CN bands. In discharge tubes this amount of energy is available and the CN bands are readily produced. In the plasma the CN violet system was one of the most intense systems observed at both atmospheric and low pressure. It is difficult to see how nitrogen got into the plasma when the plasma was operated with the inert gas in the system at atmospheric pressure, for the gas introduction system was constructed of Pyrex glass tubing with several ground glass joints. The only part open to the atmosphere was the end of the tube approximately one foot on the exhaust side of the working coil of the generator and a steady flow of argon gas was continually being ejected from this open end. Thus, the pressure within the glass system was higher than atmospheric pressure and any leak should have been to the atmospheric, not from the atmosphere. Nitrogen, somehow, entered the plasma, became activated, and reacted with the carbon to produce CN violet radiation.

Another interesting point is the complete absence of the CN red system. This system is found at longer wavelengths and thus should require less energy for excitation. Several points corresponding to known intense CN red radiation were checked in the spectra but no bands were found.

With such intense CN violet radiation, it seems that the CN red should also appear since these systems generally occur together. In order to show that the spectrograph and optical system would photograph CN red radiation, a carbon arc was burned in air and its spectrum photographed using the same apparatus. This process is known to produce CN red radiation and indeed, this species was identified by the band at 6355.1 A on the film. This shows that the apparatus was able to photograph the CN red radiation if it was present in high enough concentration.

The CH 4300 A system and the 3900 A system generally occur along with the C_2 Swan system. (10) This was the case in this investigation with the exception that the CH system was absent when carbon tetrachloride was the sample. However, neither the C_2 Swan system nor the CH system were observed at low pressure and again, this does not agree with previous observations for other methods of excitation. (4)(10) The CH 3143 A system was not observed probably due to the absorption of this radiation by the external optical system.

The CO Angstrom system was readily observed in all spectra recorded at low pressures only. This system requires more than ten electron volts for excitation and thus is not observed in emission in flames. This system is readily observed in the positive column of an uncondensed discharge. (4) Since the plasma contains sufficient energy to activate molecular nitrogen (approximately ten electron volts), it seems that some CO would also be excited and emit radiation at atmospheric pressure, however CO emission occured only at low pressures.

The N_2 Second Positive system is readily observed at low pressure in the plasma. Presumably, the nitrogen concentration in the plasma at low pressure is relatively large. This then would explain the observed radiation. However, nitrogen must also be present at atmospheric pressure since CN violet radiation of high intensity is observed. This N_2 system is also excited in the positive column of discharge tubes containing nitrogen.

The NH 3360 A system occurs under a wide variety of conditions; in certain flames, in discharge tubes, and in low pressure arcs all containing nitrogen and hydrogen. (3) Thus, the appearance of this system can be attributed to the reaction of activated nitrogen with hydrogen.

For other comparisons of molecular emission spectra using the radio-frequency plasma torch for excitation, and particularly a comparison with flame excitation, see Reference (6).

CHAPTER VI

CONCLUSION

The presence or absence of various species under plasma excitation does not correspond with results for either flame excitation or discharge tube excitation. For example, the CO Angstrom system is not seen in flames but it is readily excited in the low pressure plasma. Also, the CN system is seen only in flames containing nitrogen in the combining form but it is very intense in both atmospheric and low pressure plasmas. A comparison of the conditions of plasma excitation with discharge tube excitation shows that while discharge tubes always operate under low pressure, plasmas are stable at both atmospheric and low pressure. These preliminary investigations indicate that the radio-frequency plasma torch described in this work is a unique method for the excitation of hydrocarbons in the study of molecular emission spectra.

This work also indicates that further investigations will prove to be of value. Several questions immediately come to mind. At what pressure does the C_2 molecule stop emitting and at what pressure does the CO molecule start emitting? An attempt was made to answer this question, however possibly due to the low power of the generator, the plasma could not be stabilized at any intermediate pressures. Possibly a variable power output generator would enable one to increase the output as one lowered the pressure and thus investigate the intermediate pressure range from

600 mm to 100 mm of Hg.

Another question concerns the absence of the CN red radiation. It is not clear why this system should be absent, especially when the CN violet radiation is so intense. Finally, it becomes difficult to explain the complete absence of the C_2 radiation at low pressure again, when the CN violet is so intense.

Thus, it is suggested that a variety of samples be investigated by plasma excitation. These samples could include halogen or nitrogen containing hydrocarbons as well as aromatic hydrocarbons. The samples could be excited at a series of pressures and at a variety of levels of power output of the generator. With further investigation, this could possibly lead to a better understanding of the mechanism of formation and excitation of molecular emitting species.

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