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The Study of Gas Decomposition Due to Laser Stimulation

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THE STUDY OF GAS DECOMPOSITION
DUE TO LASER STIMULATION

by

James A. ^{Arthur} Burke CC 1977

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Submitted in partial fulfillment
of the requirements for
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ABSTRACT

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A survey of various gases known to emit radiation when pumped with a laser was undertaken to discover whether or not these gases would decompose as a result of the laser stimulation. A literature search provided some previous work in this area but left many gases unstudied.

Methanol, 1,1-difluoroethylene, ethanol, methylene chloride and methyl iodide were subjected to laser irradiation. Using an infrared spectrophotometer as a detector, none of these five gases showed clear evidence of decomposition. Because of inherent limitations of the IR detection system, a mass spectrometer was put into operation. Calibration of this instrument was performed. Results of the calibration suggest that the mass spectrometer would greatly improve the original experimental setup.

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Since 1960 the field of chemistry has had available a new method of generating electromagnetic radiation. It was during this year that the first laser (Light Amplification by Stimulated Emission of Radiation) was put into operation. This new tool offered a source for high powered, monochromatic, directional beams of electromagnetic radiation in the submillimeter wavelength region. Much work is being done at present in the area of discovering different materials which will act as lasers. This project is concerned with the approach of "pumping" various gases with a CO₂ laser, with intentions of having the gases act as lasers. However, the emphasis will not be on determining optimum conditions for producing laser action, but rather, determining whether or not the gases tested will undergo decomposition as a result of excitation by a CO₂ laser.

The laser is an electromagnetic radiation generator, so an examination of the theory of electromagnetic radiation is in order. There are two coexisting theories pertaining to electromagnetic radiation, the first of which considers the radiation to have a wavelike nature. Each wave consists of an alternating electric field with an associated perpendicularly oriented magnetic field, as shown in Figure 1. The intimate relationship between electric and magnetic fields has been developed over the last one hundred years by such men as Oersted, Ampere, Henry, Faraday, Kelvin, Maxwell and Hertz, with Hertz

actually producing and confirming the existence of radiation waves. Because it is the electric field which interacts

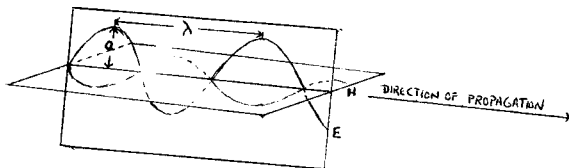


FIGURE 1
ELECTRIC VECTOR E AND MAGNETIC VECTOR H OF A PLANE POLARIZED ELECTROMAGNETIC WAVE¹
with the electrons in matter, the electric field will be discussed more fully.

The major parameters of electromagnetic waves are frequency, velocity, wavelength and amplitude. The frequency, ν , is the number of oscillations of the field that occur per second. This parameter is determined by the source of the waves and is independent of the media through which the wave travels. The velocity, v , is the rate at which the wave front moves through a medium and is dependent upon both the medium and the frequency. The linear distance between corresponding points on two adjacent cycles of the wave is designated as the wavelength, which is given the symbol λ . Multiplying the frequency by the wavelength gives the velocity of the radiation.

$$(i) \quad v = \nu \lambda$$

In any medium other than a vacuum, the rate of propagation (velocity) is less than in the vacuum because of interaction between the radiation and the bound electrons of the medium. Since the frequency is invariant, the wavelength must decrease. A fourth parameter is the amplitude which is a

measure of the field strength. When dealing with infrared laser light the frequencies are in the range of 10^{10} to 10^{14} cycles per second. Wavelengths are on the order of 10^{-2} to 10^{-3} cm.^{2,3}

While the wave model explains the occurrence of phenomenon such as reflection, refraction and diffraction, this model does not explain blackbody radiation of the photoelectric effect. The photoelectric effect is the ejection of electrons from a metallic surface which is exposed to electromagnetic radiation. However, the radiation must be of a certain minimum energy to cause ejection, with the minimum level dependent upon the metal. Energy below the minimum level will eject no electrons. Also, the energy of the emitted electrons varies with frequency but remains constant regardless of the radiation beam intensity. Because of this behavior, an energy packet (or particle) model was devised. The packets of energy are called photons. The energy of a photon is given by:

$$(2) \quad E = h\nu$$

where h is Plank's constant and ν is frequency. As one photon of sufficient energy ejects one electron, an increase in beam intensity causes not a change in electron energy but an increase in the number of ejected electrons.^{4,5,6} There is no known phenomenon which requires the use of both theories at the same time.

The ability of a material to absorb and emit photons is related to the energy levels of the material. The levels of interest are designated as electronic, vibrational

rotational and translational. The level of lowest energy is defined as the ground state, with all other levels designated as excited levels. Electronic energy levels are widely spaced and we may assume that we will be dealing with only ground electronic levels when the molecules are at room temperature and atmospheric pressure. Each electronic level has associated with it various vibrational energy levels. Associated with each vibrational level are various rotational levels. Translational energy levels are usually so closely spaced that they cannot be individually distinguished.

Absorption may occur when a photon contains energy equal to the difference between two energy levels of a molecule where transition is allowed by selection rules. The energy of the radiation absorbed is given by:

$$(3) \quad h\nu = E_2 - E_1$$

where E_1 and E_2 are the energies of the states involved in the transition. The selection rules regulating transitions of interest to us are:

$$(4a) \quad \Delta \text{VIBRATIONAL LEVEL} = 1$$

$$(4b) \quad \Delta \text{ROTATIONAL LEVEL} = \pm 1$$

The physical basis for the selection rules is that the transition must involve a nonzero displacement of electronic charge. These rules are not absolute but will provide some guidance as to whether a transition between two specified energy levels should be expected. The probability of absorption taking place for two specific levels is:

$$(5) \quad P_{mn} = U_{\nu} B_{mn}$$

where \mathcal{U}_ν is the radiation density at the frequency that corresponds to the energy difference of the levels m and n ($m < n$) and B_{nm} is a constant determined by the system. If the energy of the photon or series of photons absorbed is large enough, the energy in the vibrational degrees of freedom for a certain bond may be greater than the bond's dissociation energy. This results in bond breakage, also known as decomposition.⁷

Following the above selection rules, an atomic system in an excited level may emit radiation so that the system is reduced to a lower excited level or the ground level. One process of emission is the spontaneous release of a photon by an excited system. The probability that a system in level n will spontaneously change to a lower level m within a unit time is denoted by A_{nm} . This radiation is from an incoherent source and cannot be used in amplification. Emission can also occur under stimulation by electromagnetic radiation of appropriate frequency. The overall probability that a transition from n to m will occur is given by:

$$(6) \quad P_{nm} = A_{nm} + \mathcal{U}_\nu B_{nm}$$

where \mathcal{U}_ν is the radiation density at the frequency that corresponds to the difference of the levels n and m ($m < n$) and B_{nm} is a constant determined by the system. As a result of selection rules, a system may get into an excited level from which it will have difficulty returning to the

ground level. A level from which all transitions to lower energy levels are forbidden is known as a metastable level. Because transitions to lower energy levels are forbidden, systems will remain longer in a metastable state than in another excited state.⁸

The longer than normal lifetime of a system in a metastable state allows a build up of systems in that state. This is the basis of a population inversion of systems which is necessary for laser action. Given a large number of atoms (N_0), it is known that in thermal equilibrium the atoms will be distributed among the different levels according to Boltzmann's law:

$$(7) \quad N_n = \frac{N_0 e^{-E_n/kT}}{\sum e^{-E_0/kT}}$$

where N_n is the number of atoms in the excited level n .

At moderate temperatures very few atoms will occupy even the first excited level compared to the number present in the ground state because $e^{-E_n/kT}$ is very small in comparison to $e^{-E_0/kT}$. If a beam of electromagnetic radiation is passed through such a system, the incident beam will suffer a net loss of photons because the rate of absorption is greater than the rate of emission. If we are in some way able to achieve population inversion ($N_n > N_m$) the incident beam for radiation of frequency

$$(8) \quad \nu = (E_2 - E_1)/h$$

will be amplified. Amplification by stimulated emission leads to laser action.⁹

Some of the methods of obtaining a population

inversion are listed below:

- 1) The material may be pumped by another laser. The laser provides a source of electromagnetic energy of a particular frequency which the material absorbs. Pumping refers to the redistribution towards higher energy levels. The process of pumping can also be initiated by a xenon flash tube.
- 2) An electric discharge will cause an increase in the number of collisions among gas molecules. By using the correct gas, the collisions can cause an energy transfer from one molecule to another in the direction of higher energy levels.
- 3) Applying a magnetic field may reorient the spin of orbiting electrons. In order to change spin orientation an electron must either absorb or emit energy. This technique is used primarily with solid lasers.
- 4) The higher energy particles of a gas may be separated from the lower energy particles by passing the gas through an electric current.¹⁰

The CO_2 laser, which is frequently used as the pumping laser, uses the first excited symmetric stretching state of CO_2 (100), the second excited bending state (020), and the first excited antisymmetric stretching state (001) to achieve population inversion. These states have frequencies of 1388 cm^{-1} , 1200 cm^{-1} and 2349 cm^{-1} respectively in comparison to the ground state (000). The transitions are taking place between the rotational sublevels of the vibrational levels shown in Figure 2. The 001 to 020 transition

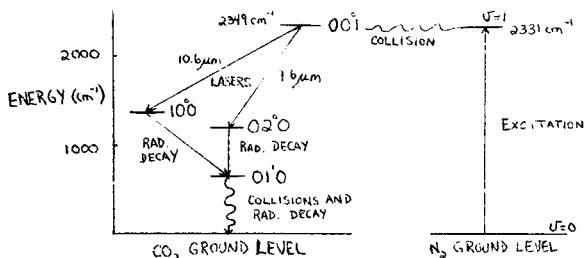


FIGURE 2
ENERGY LEVEL DIAGRAM OF VIBRATIONAL LEVELS OF CO₂ AND N₂ 11

produces radiation at 9.6μm, while the 00¹ to 1⁰ transition radiates around 10.6μm. These two pathways are in competition, with the 00¹ to 1⁰ transition having the faster rate.

The population inversion in the 00¹ level is brought about by the following process. Electron collisions in the electric discharge causes the excitation of CO₂ molecules to various 00⁰_v levels. When a molecule in one of these excited states collides with a molecule in the ground state, a 00¹ molecule and a 00⁰_{v-1} molecule result. Ultimately most of the 00⁰_v molecules are converted to 00¹ molecules.

At the same time similar emissions are taking place on the other ladders, with molecules accumulating in the 1⁰ and 02⁰ levels. One of the advantages of the 00¹ level is that electron collisions are more likely to excite asymmetric stretch vibrations than symmetric vibrations. Also, the 1⁰ and 02⁰ levels drain quickly to the 01⁰ level so these levels can be used as terminal laser levels. The draining of the 01⁰ back to the ground level occurs at a rate slower than the rates of the other processes. This

rate may be increased by the presence of He in the gas chamber and keeping the laser tube walls cool. As the electrons return to the ground level they are then ready for reexcitation and continuation of the laser action.

The N_2 gas is added to further the $00\bar{1}$ population inversion. The $v=1$ vibrational level of N_2 is populated much the same way the $00\bar{1}$ level of CO_2 is populated. When an excited, $v=1$ N_2 molecule collides with a ground state CO_2 molecule, an efficient energy transfer occurs. This results in the returning of the excited N_2 molecule to the ground state and excitation of ground state CO_2 molecules to the $00\bar{1}$ level.

Both the $9.6\mu m$ and $10.6\mu m$ laser transitions may occur over a number of rotational levels. Usually laser action occurs for only one rotational transition. Because of the rapid thermalization of the rotational sublevels, they replenish each other when one is depleted. Therefore, all levels tend to lose their populations by transferring to the favored level which first started to lase. We can tune which rotational transition will be favored to lase primarily by changing the cavity length. It is through this adjustment that we can use the CO_2 laser to pump various other gases to population inversions.^{12,13}

Besides the population inversion, the other major aspect of laser technology is the optical resonator. The optical resonator cavity provides the necessary regenerative feedback of the stimulated emission to achieve high intensities

of coherent collimated radiation. The principles behind the resonant cavity are the coherence and monochromatic nature of laser light. The coherence is dependent on the monochromatic characteristics of the radiation. Monochromatic radiation is radiation of a single frequency. Although the laser light is not truly monochromatic, it is much closer to monochromatic than any other radiation source available. The other condition for coherence is that the phase relationship between the waves must be constant at all times. The waves in the laser are more coherent than waves from other radiation sources. Thus, the waves in the laser add to or reinforce each other and do not alter their direction of propagation or frequency of oscillation.

The resonant cavity is constructed so as to take advantage of these characteristics of laser light. The cavity length must be an integral number of half wavelengths of the radiation for the necessary constructive interference

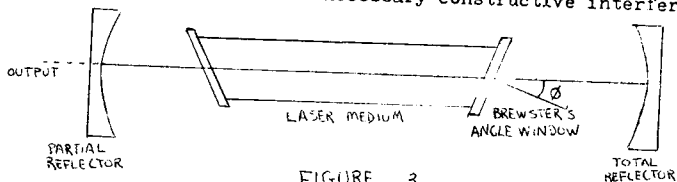


FIGURE 3
RESONANT CAVITY OF A GAS LASER¹⁴

to occur. The light wave is reflected back and forth between the mirrors many thousands of times with coherent amplification occurring on each pass of the wavefront through the cavity. The partial reflector then allows some of the radiation to escape from the resonant cavity. The mirror

and cavity setup provides the laser with directional radiation beams of high intensity. The Brewster's angle windows shown in Figure 3 reduce radiation losses due to reflection. This enables us to place the mirrors outside the laser tube where they are less likely to be damaged by the discharge and where they can be easily adjusted.^{15,16,17}

Since 1960 laser technology has been progressing at a tremendous rate. The three primary groups of lasers are solid state, semi-conductor and gas. Solid state lasers usually have a lasing material of solid or ionic crystals which is optically pumped. The most important solid laser is the ruby laser shown in Figure 4. The ruby crystal acts

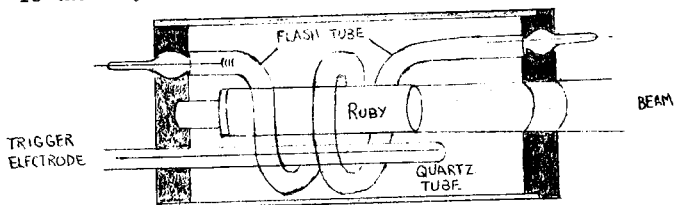


FIGURE 4
RUBY LASER¹⁸

as the resonator cavity of the gas laser. The ends of the crystal are ground and polished parallel to each other and are provided with a reflective coating which permits only a small fraction of the incident light to pass through. The ruby laser is an example of a three level system, as shown in Figure 5. The three level system requires a large pumping energy to maintain population inversion as level 1 is acting as both the ground state and the terminal state.

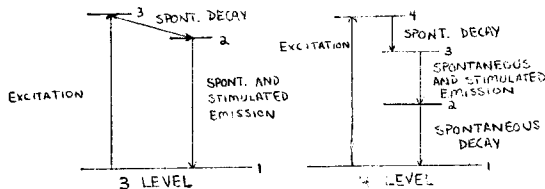


FIGURE 5
ENERGY LEVEL DIAGRAMS¹⁹

The four level system eliminates this problem by providing a population inversion between levels 2 and 3, with the ground state acting merely as an electron collector. Most of the solid state lasers, with the exception of the ruby laser, are of the four level type. The principal disadvantage of solid lasers is the poor light output to electrical energy input ratio. This low efficiency is caused primarily by a poor spectral matchup between the pump output and the laser absorption bands.^{20,21}

Another group of lasers are the semi-conductor lasers. As shown in Figure 6, the application of an electric current causes electrons to be injected into the N type region. At the junction these electrons combine with the "holes" in the P type region and energy is given up in the process in the form of light photons. Population inversion is attained

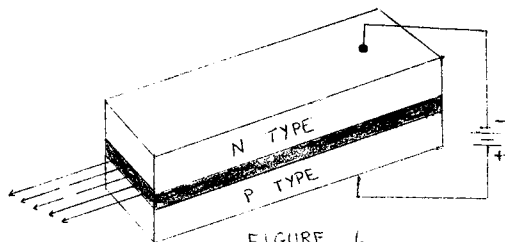


FIGURE 6
A SEMICONDUCTOR LASER²²

when there are more injected electrons than holes in the P type region. By polishing opposite faces of the diode a resonant cavity is formed which results in stimulation of photon release. An important feature of these lasers is that the wavelength of laser radiation emitted can be adjusted by varying the composition of the semi-conductor.^{23,24}

There are, of course, many other types of lasers and countless variations of each type. These lasers have been put to work in many fields and are performing a tremendous variety of tasks. Many of the applications require the high amounts of energy available in short time intervals provided by the laser. For example, lasers are being used to perform precision welding and drilling, primarily in the micro range. Powerful lasers have been developed which can drill through diamond. Besides these applications, the laser is becoming an important tool in the fields of chemistry and biology. The monochromatic nature of the laser radiation is suited to study of molecular structure and chemical reactions. The medical field is now using the laser for thermal coagulation, cauterization and tissue destruction. Physics and astronomy are finding lasers useful in distance and velocity determinations. The high degree of directionality of the laser beam is exploited for these applications. Yet another potential is the communications field. The important principle here is that the amount of information which can be carried on an electromagnetic wave increases as the frequency of the radiation increases. Since the laser radiation is of higher frequency than existing communications systems, there would be a tremendous increase in the number

of channels available should this potential be developed. All of these present and potential applications of laser systems show the need for continued development of laser technology.²⁵

PREVIOUS WORK ON DECOMPOSITION

A search of published material pertaining to laser research was conducted in order to discover references to gas decomposition due to laser stimulation. Many of the researchers were attempting to determine whether a decomposition reaction was thermal or photochemical. However, the thrust of this research was to determine whether or not decomposition itself would occur and was not directed to the mechanism of decomposition. Of primary concern was the possibility of using the sample gas in a sealed laser. Decomposition of the gas would soon destroy the efficiency of such a sealed laser.

A thorough study of decomposition of ethyl chloride due to laser irradiation was performed by Bailey, Cruickshank, et al²⁶. Their experimental pressures ranged from .2 to 100 torr, with power input of 105-160W from a continuous wave CO₂ laser. They assumed a fast rate of redistribution of energy among various degrees of freedom within a molecule. The low pressures and high power levels were used so that the vibration level near the dissociation limit could be reached before the redistribution of energy occurred. The CO₂ laser line used was at 972 cm⁻¹ which corresponds to an ethyl chloride C-C stretching band. After lasing, ethyl chloride, C₂H₄, HCl, CH₄ and C₂H₂ were identified in the sample chamber. At pressures over approximately 80 torr decomposition was immediate at a cell temperature of 300 K. At lower pressures an induction period was seen and has

been attributed to the inhibiting effect of "cold" ethyl chloride diffusing into the path of the laser beam.

Muller and Flesher^{27,28} have done work with various combinations of H_2O , D_2O and CH_3CN . A flowing vapor system with a dc discharge was used to create a laser beam. It was noted that when CH_3CN was used as the flowing vapor that the walls of the discharge tube became opaque with a brown deposit which was thickest near the cathode end. Subsequent use of H_2O as the flowing vapor gradually removed the deposit. When H_2O or D_2O was used in conjunction with CH_3CN , strong laser action was obtained but contamination was greatly reduced. Muller and Flesher have postulated that the laser action is due to a rotational transition of the CN radical, which must be formed from decomposition of CH_3CN in sufficient amounts to allow laser action.

Atomic iodine emission has been detected by Kasper, Parker and Pimentel.^{29,30} The experimental conditions used in their work included flash photolysis on the order of 2500-3000 Joules and sample pressures of 10 to 81 torr. A flash photolysis of 2600 Joules caused 75% decomposition of an 81 torr sample of CF_3I . For lower power levels (320 Joules) 3% decomposition was detected. Similar results were obtained for CH_3I .

Cuellar, Parker and Pimentel³¹ have reported laser emission from rotational transitions of HF formed through elimination reactions, both from chemically activated

CH_3CF_3 and from photoexcited CH_2CF_2 . Chemical activation of CH_3CF_3 was accomplished through flash photolysis of CH_3I and CF_3I . Photoexcitation of 1,1-difluoroethylene was performed on a 62 torr sample of $\text{CH}_2\text{CF}_2\text{:Ar}$ in a 1:100 mixture. Thermal elimination of HF from $\text{CH}_3\text{CH}_2\text{F}$ and CH_3CHF_2 at temperatures between 425 and 525 C has also been documented in publications.^{32,33}

Albert Adelman³⁴ has produced evidence of break down of organic vapors at pressures ranging from 90 to 180 torr. The laser used to produce the decomposition was a pulsed ruby laser. Adelman presents the following table of his results.

TABLE 1

MATERIAL	PRESSURE (torr)	SPECIES ABSORBED IN EMISSION
CCl_4	91	C_2 , C , C^+ , C^{+2} , Cl^+
CHCl_3	160	C_2 , C , C^+ , C^{+2} , Cl^+
CH_3OH	93	C_2 , C , C^+ , C^{+2} , O^+
Hexane	120	C_2 , C , C^+ , C^{+2}
Acetone	180	C_2 , C , C^+ , C^{+2} , O^+

A larger organic molecule, 1 Limonene, has been irradiated at a pressure of 2 torr in a 4 meter long irradiation cell with a 5W, 10.6 μm CO_2 continuous wave laser beam. Yagev, Loewenstein and Amar³⁵ found a number of cleavage products after the laser stimulation. Isoprene was the major product, but benzene, toluene, ethyl benzene, methyl ethyl benzene and smaller compounds were also detected. While 1 limonene is not one of the gases known to emit radiation as a result of optical pumping, evidence of its

decomposition indicates the need for more work concerning the stability of other organic molecules undergoing laser stimulation.

Pyrolysis of dimethyl ether at temperatures between 750 and 820 K has also been documented.³⁶ There is a possibility that high power laser irradiation could cause decomposition along the same lines as the pyrolysis.

Work is currently being done at Union College on the decomposition of freons. Using sample pressures of 1 to 100 torr and input power of 20W from a CO₂ laser, cleavage of freons has been detected.³⁷

A summary of the information concerning decomposition of gases due to laser stimulation is presented in Table 2.

TABLE 2

GAS	STIMULATION METHOD	DECOMPOSITION OBSERVED	REF.
CH ₃ CH ₂ Cl	105-160W continuous wave CO ₂ laser	cleavage of the C-C bond	26
CH ₃ CN	dc discharge, flowing vapor	CN radical	27, 28
CH ₃ I	flash photolysis	atomic iodine	29, 30
CH ₃ CF ₃	quartz flash tube	HF	31
CH ₂ CF ₂	quartz flash tube	HF	31

SCOPE

The intent of this research was to perform a study of gases which are known to emit radiation when pumped with an infrared laser. The major area of study was to determine which of these gases would decompose as a result of absorbance of laser radiation. The gases of interest were CH_3F , $\text{C}^{13}\text{H}_3\text{F}$, CH_3CF_3 , CH_3CHF_2 , $\text{CH}_3\text{CH}_2\text{F}$, CH_3CCH , CH_3OCH_3 , CH_3OH , CH_3OD , CD_3OD , CH_3CN , CH_3CN_2 , CH_3Cl , CH_3Br , CH_3I , HCOOH , CH_2Cl_2 , CH_2CHCN , CH_2CF_2 , CH_2CHCl , $\text{C}_2\text{H}_4(\text{OH})_2$, $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{Cl}$, NH_3 , O_3 , and D_2O .

EXPERIMENTAL PROCEDURES

THE SAMPLE CELL

The sample cell is diagramed in Figures 7A and 7B. Because of the special requirements of the cell's design it was obtained from a glass blower. The cell dimensions allow for a 10 cm pathlength for both the infrared detector and the laser beam. The 19/38 ground glass fitting permits attachment of the cell to the vacuum line apparatus. The two rubber seals shown on the left in Figure 7A make a permanent seal between the sample cell stopcock arm and the main body of the cell. The rubber seal on the right in Figure 7A only creates a seal when the sample cell stopcock is fully tightened. The larger two windows were KBr. These windows provide a path for the IR detector. They were 4.9 cm in diameter and .7 cm thick. The window through which the laser beam enters the cell was CsBr, while the exit window was NaCl. NaCl and KBr windows were found to be prone to cracking when used as the laser entry window. The CsBr window was 3.0 X 4.5 cm and .3 cm thick. The laser exit window was 2.5 cm in diameter and .6 cm thick. All four windows were affixed to the main body of the cell with a silicone rubber sealant.

The windows became clouded after several weeks due to water absorption and, therefore, had to be periodically polished. The windows were removed by placing the window of interest and arm of the cell in benzene for approximately twelve hours. After soaking, the window was easily removed

and the excess sealant was cleaned off the sample cell with a sharp knife or single edge razor blade. Using rubber gloves so that moisture from the hands did not absorb on the window, the window was rough polished on a glass surface with ethanol and a coarse abrasive. Fine polishing was achieved with ethanol, rouge and a rouge cloth. The window was then recemented to the sample cell. Twelve hours drying time was required and care had to be taken to insure that the window was parallel to the table top to avoid the problem of slippage before the sealant set. The windows remained usable for longer periods of time when the cell was stored in a desiccator when not in use.

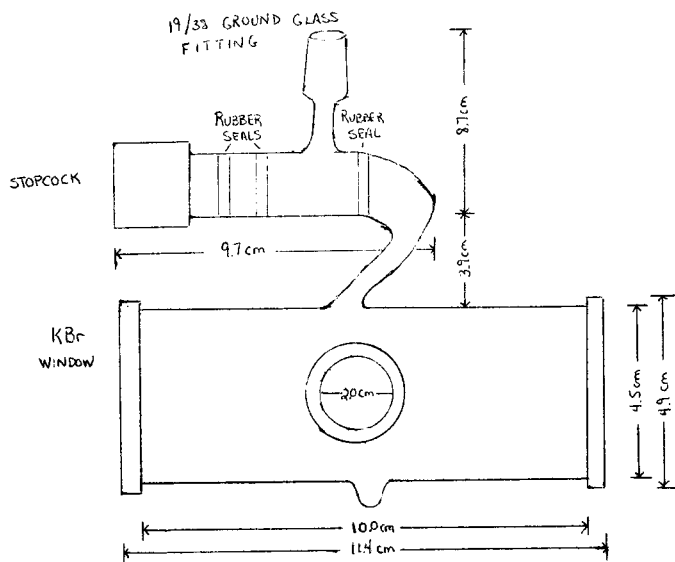


FIGURE 7A
THE SAMPLE CELL - FRONT VIEW

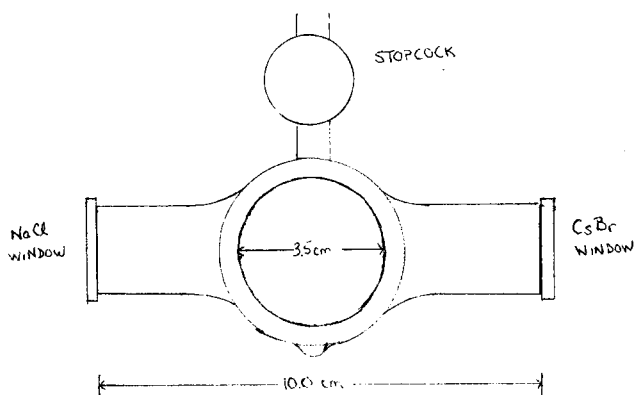


FIGURE 7B
THE SAMPLE CELL - SIDE VIEW

THE VACUUM LINE

Components:

Glass apparatus shown in Figure 8
Model 1402 Duo Seal Vacuum Pump
3 Dewar flasks and liquid nitrogen
NRC 801 Micron meter
Thermocouple
Teflon stopcocks

Pump down of the system shown in Figure 8 is achieved by means of two liquid nitrogen traps and a mechanical pump in series. The liquid nitrogen traps cause condensation of volatile materials which are drawn to the traps by the mechanical pump. For initial pump down all stopcocks, with the exception of stopcock 10, were closed. Stopcocks 1, 3, 4, 5, 11, 12, and 18 were then opened in the order listed, with a three minute interval allowed between the opening of each stopcock. The establishment of a vacuum was determined by reading the NRC 801 micron meter. A reading of less than 20 microns indicated a good vacuum.

The system was now ready for sample introduction. There were two similar procedures for getting a sample in the line. The procedure used depended on whether the sample was a liquid or a gas. For a liquid sample, approximately 1 to 10 ml of the sample was placed into a small bulb which was fitted with a 19/38 ground glass joint. The bulb could be attached at any point on the line which was open to the atmosphere and had the correct female fitting. However, the positions of stopcocks 15 and 16 were used most frequently. The sample was then frozen using liquid nitrogen in a Dewar flask. The stopcock immediately above the bulb

was opened and several minutes of pumping were allowed to reestablish the vacuum. The stopcock was then closed and the liquid allowed to melt. The sample was once again frozen, vacuum pumped and allowed to melt. This procedure is known as degassing and results in the removal of dissolved gases in the sample.

The sample now had to be stored in the vacuum line. A Dewar flask filled with liquid nitrogen was placed around the glass tubing between stopcocks 4 and 5 or 11 and 12 or around the extension at the bottom of the storage bulb. Stopcock 3 was closed so that the sample would not be pumped out of the system. The stopcock immediately above the sample bulb was opened. Because of the low pressure region in the liquid nitrogen trap, the sample moved from the sample bulb to the storage area. After transfer was complete, stopcock 3 was opened to obtain a final degassing. The final step was to close the stopcock(s) surrounding the storage area and remove the liquid nitrogen trap.

For a gaseous sample, the gas container, usually a lecture bottle, was attached to the vacuum line by means of tubing running from the regulator on the tank to the fitting at stopcock 13. This fitting was of the ball and joint type. Stopcock 13 was opened to draw any gas out of the tubing and then was reclosed. Stopcock 3 was closed and a liquid nitrogen trap placed around a storage area. Stopcock 13 was reopened and the regulator turned on. When sufficient gas was in the system the regulator was shut off

and stopcock 13 closed. Degassing was then performed at the storage area.

The sample gas or liquid now had to be transferred to the sample cell at experimental pressures. The sample cell was usually attached to the vacuum line at the fitting below stopcock 15. With stopcock 3 in an open position, both the cell stopcock and stopcock 15 were opened. Attainment of a vacuum can again be determined by readings from the micron meter. For sample pressures of greater than 2 torr the following procedure was used. Stopcock 3 was closed and a reading taken on the mercury scale. One of the stopcocks surrounding the storage area was carefully opened, allowing the desired pressure to enter the rest of the system. The stopcock was then immediately reclosed and a second reading of the mercury was taken after a several minute delay which permitted equilibration to occur. The sample cell stopcock and stopcock 15 were then closed. The difference between the two mercury readings gives the pressure in the sample cell.

If the gas now remaining in the line was to be saved, the storage area had to be frozen with liquid nitrogen. One of the stopcocks surrounding the storage area was opened. The micron meter indicated when most of the gas was restored and the storage stopcock was closed. Due to the vacuum established between the sample cell and stopcock 15 removal of the cell from the line was difficult. Stopcocks 12 and 18 had to be closed and stopcock 16 opened. The section of

the vacuum line between stopcocks 12 and 18 was now at atmospheric pressure. Stopcock 15 was opened and the sample cell could be carefully detached from the line. By closing Stopcocks 15 and 16 and opening stopcock 18 the system was once again pumped down to a vacuum. If saving the gas was unimportant, one can immediately proceed to the procedure for detaching the sample cell from the line.

For sample pressures of less than 2 torr the mercury readings were too inaccurate to provide experimentally acceptable values. Instead, a gas was stored between stopcocks 11 and 12. Stopcocks 3, 4, 5, and 18 were closed and the sample cell attached to the fitting below stopcock 15. The sample cell must be evacuated prior to the closing of the stopcocks. A pressure reading was taken on the mercury scale. Stopcock 12 was opened and then reclosed. This allowed some of the gas to expand into the line between stopcocks 12 and 18. A second pressure reading was taken. Stopcock 15 was opened permitting the gas to enter the area between the stopcock and the sample cell stopcock. A third pressure reading was taken. This procedure of opening a stopcock and taking a pressure reading was continued until the sample cell stopcock and stopcocks 18, 4 and 5 were opened. This total procedure was repeated five times to insure accuracy. Ratios of the pressures in various sections of the line can then be calculated. Table 3 shows the experimental ratios obtained for our system.

TABLE 3

SECTION OF THE VACUUM LINE	RELATIVE VOLUME
12 - 18; 13 through 17 closed	1.00
12 - 4; 13 through 17 and 3 closed	1.06
12 - 5; 13 through 17 and 3 closed	1.19
12 - 11; 13 through 17, 3 and 6 through 10 closed	1.51
12 - 18; 15 open, cell stopcock closed	1.04
12 - 18; 15 and cell stopcock open	1.29

To obtain a low pressure in the sample cell the entire system, excluding the storage area, was evacuated. Stopcocks 3 and 5 were closed, while stopcocks 4 and 18 were open. A suitable pressure was expanded into the line between stopcocks 12 and 5. Stopcock 4 was then closed and stopcock 3 opened until vacuum was reestablished between stopcocks 3 and 12. Stopcock 3 was closed and 4 opened. This allowed the gas trapped between stopcocks 4 and 5 to expand into the sample cell. The sample cell stopcock was then closed. The pressure in the cell can be calculated using the various volume ratios shown in Table 3.

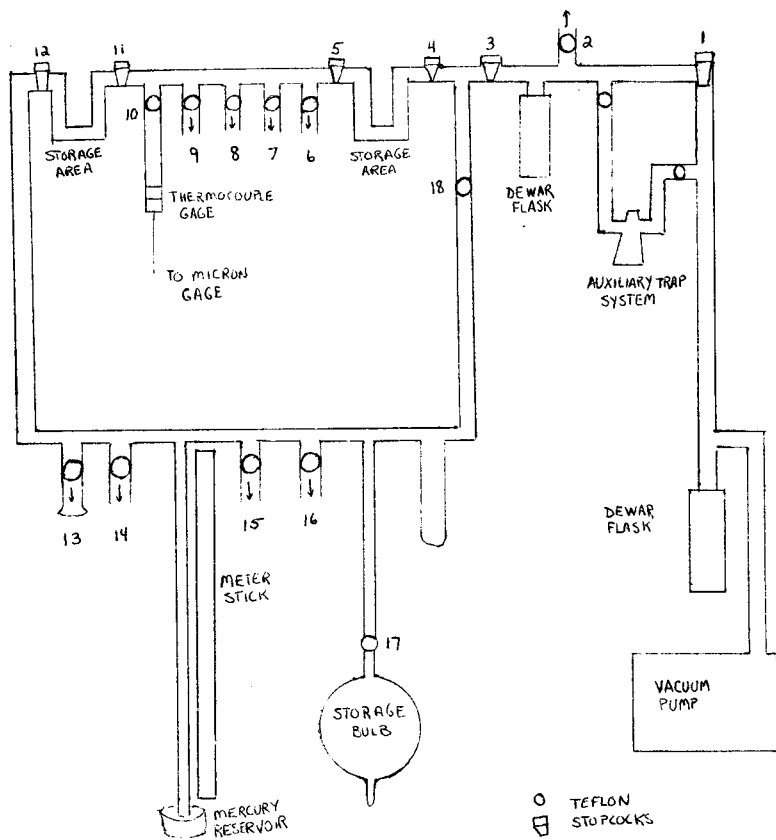


FIGURE 8
THE VACUUM LINE

THE LASER AND INFRARED DETECTOR SYSTEM

Components:

Molelectron Model C25C Infrared Gas Laser
Neslab RTE-4 Water Circulator
Molelectron Model CPS Power Supply
Vacuum Pump
Chopper
Coherent Radiation Palo Alto Model 201 Detector
Ithaco Dynatrac 391 Lock In Amplifier
Jarrell Ash Model 82-000SER Monochromator
Molelectron detector
Perkin Elmer Model 21 Infrared Spectrophotometer
Spectra Physics 155 Helium Neon Laser
NaCl partial reflecting window
Gold Plate Mirror
Mirror and Ring Stand Assembly

The main advantage of the system shown in Figure 9, when used in conjunction with the specially designed sample cell previously described, was the ability to operate both the laser and the IR detector simultaneously. The laser was a continuous wave model which could achieve CO_2 emission of greater than 20W on many of the tunable wavelengths between 9.17 to 9.80 and 10.13 to 10.9 μm . The power stability of the laser was rated at $\pm 2\%$ for an operating time of four hours. The procedure for tuning the laser to the desired wavelength can be found in the Molelectron laser operation manual.

The mirror and ring stand assembly was aligned so that the laser beam would pass through the CsBr window of the sample cell. If the beam hit the edge of the window or the sealant used to affix the window to the cell, cracking of the window was likely to follow. The CO_2 laser was not on during the mirror alignment procedure. The sample cell was

placed in the holder so that the IR detector beam would pass through the two KBr windows. The small red helium-neon laser was turned on and aligned in such a manner that the beam passed through the center of the NaCl and CsBr windows. The sample cell was now removed from the holder. The mirror and ring stand assembly was placed on the table top and aligned so the the helium-neon laser beam reflected off the mirror into the main laser window. The beam had to reflect off the CO₂ laser window, reflect off the mirror a second time and be directed back to the helium-neon laser orifice for the alignment to be correct. This procedure assures that when the main laser is turned on the beam will pass through the CsBr and NaCl windows. The helium-neon laser was turned off and the sample cell replaced in the holder. Blocking bricks were positioned in front of and behind the sample cell. The chopper was turned on and the coherent radiation detector aligned to obtain a laser beam power reading. The CO₂ laser was now turned on.

While the laser power level was stabilizing, an initial IR spectrum was taken of the sample. A reading of the laser beam power was taken. The chopper was turned off and the reflecting portions were moved out of the way of the beam. The coherent radiation detector was set up behind the blocking brick in back of the sample cell. The detector was positioned carefully so that a minimum of adjustment was necessary when the blocking bricks were removed. A final check of the alignment of the laser beam and the sample cell windows was made by removing the blocking brick

but stopping the beam just in front of the cell with a hand held piece of wood. When the piece of wood was removed a stopwatch was started. Using the wood once again, the blocking brick behind the cell was removed and the radiation detector correctly positioned.

Irradiation of the sample was performed for twenty minutes with readings of the power of the laser beam passing through the cell taken every two minutes. The difference between the initial power reading and these two minute interval readings gives an indication of the laser power being absorbed by the sample gas or reflected by the cell windows. After twenty minutes of irradiation the blocking brick was placed in front of the sample cell once again. The cell was removed from the holder and ten to fifteen minutes was allowed for the gas to return to room temperature. During the cool down period the blocking brick was removed and a final power reading of the laser beam was taken to check the power stability. The blocking brick was placed in its previous position and the sample cell returned to the holder. A second IR spectrum was run on the same chart paper as the first spectrum. Using a different color ink than in the first spectrum aids in identifying the respective peaks. Comparison of the two spectra gives an indication of decomposition or stability. Decomposition will be evidenced by the reduction in one or more peak heights or the appearance of new peaks.

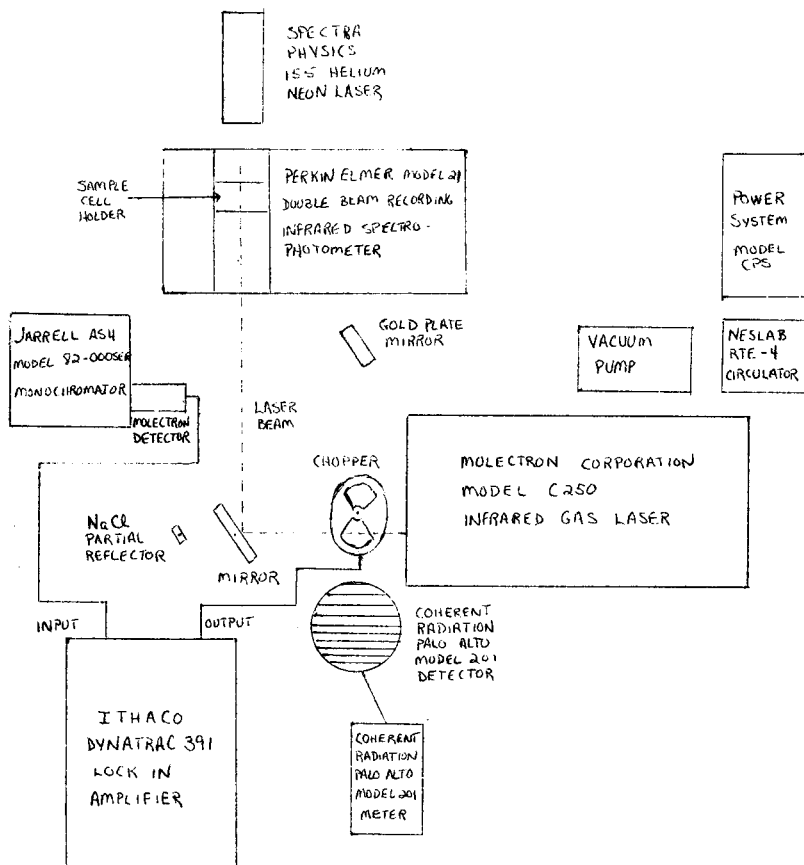


FIGURE 9
LASER AND INFRARED DETECTOR SYSTEM

RESULTS

The use of the infrared spectrophotometer resulted in limited capability of decomposition detection. A 10% decomposition of the sample would have to occur for a noticeable change in peak height to result.

The first gas tested was spectral grade methanol. The initial IR spectrum produced the following peaks: O-H stretch at 3750 cm^{-1} , C-H stretch for CH_3 at 3000 cm^{-1} , C-H bend at 1450 cm^{-1} , C-H interaction from 1300 to 1400 cm^{-1} , and C-O stretch in the $1000\text{ to }1100\text{ cm}^{-1}$ region. These experimental peaks are in agreement with a published reference.³⁸ The CO_2 laser line used for irradiation of the sample was chosen from the tables compiled by Rosenbluh, Temkin and Button.³⁹ These tables were the source of all laser lines used in this research. The criterion for choice of the line was proven laser emission when pumped with a low power continuous wave CO_2 laser and a relatively strong stimulated output. For methanol the CO_2 laser line used was the 9P(16) line which Rosenbluh had listed at an output of 1 to 3 mW with 10 to 20W of chopped CO_2 laser input. As shown in Table 4, methanol was subjected to laser stimulation at sample pressures of 41, 24, and 1 torr. No evidence of decomposition of methanol was indicated by the final spectra of any of the three experimental runs. These results imply that the CH_3OH molecule is stable under experimental conditions within experimental limits. Another CO_2 laser line which might prove of interest to work with is the 9P(36) line.

1,1-difluoroethylene was the next gas examined. It was purchased from Matheson Co. in the lecture bottle size. The initial IR spectra produced a C=C peak at 1725 cm^{-1} , a CF_2 stretching peak at 1300 cm^{-1} , a C-F interaction peak between 900 and 950 cm^{-1} , and an aliphatic C-F stretching peak at 800 cm^{-1} . These peaks closely coincided with those given in a literature spectrum.⁴⁰ The experimental CO_2 laser line for 1,1-difluoroethylene was 10P(22). The 10P(22) line had several emission lines listed in Rosenbluh's tables, with inputs of 4 to 10W and outputs of .1 to .3mW. The sample pressures used were 23, 16, 1 and .5 torr. There is a slight indication of a reduction in the C-F stretch band after laser stimulation for the 1 and .5 torr pressure runs. However, because of the IR detector limitations a positive conclusion cannot be drawn without further experiment. Other CO_2 laser lines which might be examined are the 10P(12), 10P(14), and 10P(24) lines.

Ethanol was the third gas to be tested. The ethanol used in the eight experimental runs listed in Table 4 came from three different sources. The first four experiments were performed using spectral grade ethanol obtained from a previously opened bottle. The fifth experiment used ethanol from an opened USI container. The final three runs were done using spectral grade ethanol from a previously unopened bottle. The reason for these changes can be seen in the various spectra obtained. The first five spectra all contained a peak at 1725 cm^{-1} , which may be from a C=O

impurity, and a larger than expected peak at 800 cm^{-1} . The possibility that these peaks could have been caused by contamination due to 1,1-difluoroethylene remaining in the vacuum line was checked by running an IR spectrum on the ethanol before it was placed in the line. This was done for the USI ethanol and the peak at 1725 cm^{-1} was seen. The final three spectra did not exhibit the impurity peaks and were in agreement with a literature reference.⁴¹ These spectra exhibited the following peaks: O-H stretch at 3700 cm^{-1} , C-H stretch for CH_3 at 3000 cm^{-1} , C-H interactions between 1250 and 1400 cm^{-1} , and C-O stretch between 1000 and 1100 cm^{-1} . The only CO_2 laser line listed by Rosenbluh⁴² as causing emission from ethanol was the 9P(32) line. This brings up the additional problem that the first four runs shown in Table 4 were performed at the wrong laser line. Rosenbluh listed the emission of ethanol as requiring an input of less than 20W, but this resulted in an output of only .01mW. Sample pressures of 18, 7 and 2.5 torr were used in the final three experimental runs. None gave evidence of decomposition of the ethanol. This result was to be expected as methanol showed no indication of decomposition either and the two compounds are very similar structurally.

Methylene chloride was the next gas in the study. It was purchased in liquid form from Fisher. Rosenbluh lists only the 10P(26) CO_2 laser line for use as the optical pump for methylene chloride.⁴³ This line is listed as producing

a .1mW output when stimulated with an input of less than 40W of continuous wave laser power. Experimental pressures of methylene chloride were 17.5, 7 and 292 torr. This odd progression of pressures was used because the first two spectra did not exhibit an absorption band where the CO_2 laser was supposed to be pumping. The 292 torr pressure run revealed a small band in the 900 cm^{-1} region. As a result of the smallness of this band very little of the laser power was absorbed by the gas. This can be seen by a comparison of the laser power absorbed figures given in Table 4. None of the spectra exhibited evidence of decomposition of methylene chloride. However, since very little laser power was absorbed, decomposition was not to be expected.

The final gas used in experimentation was methyl iodide. There was literature evidence that at high power inputs the molecule would decompose (see page 16). The methyl iodide was purchased from MCB in liquid form. All listings in Rosenbluh's tables of CO_2 laser pumping lines required inputs greater than the capabilities of the Molelectron laser.⁴⁴ The 10P(18) line was decided upon, although 9P(34), 10P(32), and 10P(38) would have also proved satisfactory. The first sample pressure was 6.7 torr. At this pressure the IR spectrum had virtually no peaks which could be used for identification of decomposition. There was also no evidence of a peak at the point where the CO_2 laser was supposed to be pumping the methyl iodide. No laser stimulation was

attempted and instead a sample pressure of 117 torr was used. The resulting spectra gave no indication of decomposition of CH_3I . While the peaks were larger for the larger sample pressure and there proved to be a peak in the pumping region, it was realized that even if methyl iodide did decompose the IR detector was not capable of showing it. The C-I band appears in the 500 to 600 cm^{-1} region which is out of the frequency range of the IR instrument. Should the C-I bond break, the C-H interactions which have peaks within the IR spectrophotometer's capabilities would not change much, resulting in no change in the peaks. It was now necessary to improve upon the experimental setup.

A summary of the results explained above is given in Table 4.

TABLE 4

GAS DECOMPOSITION RESULTS

GAS	SAMPLE PRESSURE (torr)	RADIATION LINE	RADIATION TIME (minutes)	LASER POWER (w) absorbed and/or reflected	EVIDENCE OF DECOMPOSITION
Methanol	24.0±.3	9P(16)	20	12.0±.5	NO
	41.0±.3	9P(16)	20	12.0±.5	NO
	1.0±.1	9P(16)	20	8.0±.5	NO
1,1-difluoro-ethylene	23.0±.3	10P(22)	20	13.0±.5	NO
	1.6±.1	10P(22)	20	6.5±.5	NO
	1.0±.1	10P(22)	20	6.0±.5	POSSIBLE
	.5±.1	10P(22)	60	5.0±.5	POSSIBLE
Ethanol	5.0±.3	9P(16)	20	8.0±.5	NO
	20.5±.3	9P(16)	20	10.0±.5	NO
	.9±.1	9P(16)	20	6.5±.5	NO
	16.5±.3	9P(16)	20	12.0±.5	NO
	18.0±.3	9P(32)	20	10.0±.5	NO
	18.0±.3	9P(32)	20	9.5±.5	NO
	7.0±.3	9P(32)	20	7.0±.5	NO
	2.5±.3	9P(32)	20	6.0±.5	NO
Methylene chloride	17.5±.3	10P(26)	20	5.0±.5	NO
	7.0±.3	10P(26)	20	4.5±.5	NO
	292.0±.3	10P(26)	20	7.5±.5	NO
Methyl iodide	6.7±.3	10P(18)	no run		
	117.0±.3	10P(18)	20	6.0±.5	NO

CONCLUSIONS

The experimental results obtained from the laser and infrared detection system revealed several shortcomings in the design of the experimental setup. The Perkin Elmer Infrared Spectrophotometer had three major limitations. Of major concern is the range of wavelengths or frequencies which can be examined with the IR detector. The PE 21 had a capability of detection from 5000 to 650 cm^{-1} . This difficulty was primarily brought out in the experimental results for CH_3I . The characteristic C-I band for this molecule occurs near 500 cm^{-1} . Should decomposition of CH_3I occur, the most probable cleavage products will be CH_3 and I. The decomposition would be evidenced by a change in the 500 cm^{-1} peak height, which is unfortunately out of the PE 21's range. The CH_3 stretch, C-H interaction, and CH_3 wag peaks at 3000, 1400, and 1250 cm^{-1} respectively will show no change from initial to final conditions if only the C-I bond is broken by the laser stimulation, as the products would have the same number of C-H bonds as the initial sample.

A second limitation involves the range of sample pressures detectable by the IR instrument. Optical pumping of gases has had best success using sample pressures on the order of mtorr. Decomposition of a gas molecule will result from the intake of enough energy from the laser beam to cause bond breakage. This means that the energy must be contained in a single vibrational level. Higher pressures

lead to an increase in collisional relaxation, a spreading of the additional energy absorbed by one molecule over several molecules through collision. Higher pressures also increase the rate of thermal conduction of heat to the cell walls. Therefore, high pressures will not be conducive to decomposition of the gas. However, as the sample pressure is reduced to normal optical pumping levels, the IR detector has fewer and fewer molecules to "look at". The peak heights become small to the point where experimental error and instrument instability do not allow accurate detection of a change in peak height from initial to final conditions. For the FE 21 the lower pressure limit which will give reasonable experimental spectra is about .75 torr depending on the sample gas.

A third problem encountered with the IR detector was a change in spectral baseline between the initial and final runs. This change made peak analysis, especially on small peaks, difficult. I assumed that the changing baseline was the result of the gas being heated by the absorption of laser energy. The assumption was based on the observation that the sample cell was warm to the touch after the lasing period. Although a ten to fifteen minute cooling period was instituted between the end of lasing and the running of the final sample spectrum, the baselines did not match. This problem might be corrected by allowing for a longer cool down period. However, as this time is increased, the effects of instrument instability and amplifier drift may become

predominant and the baselines might still not match. Further experiment is required to solve this problem.

The design of the sample cell put a further limitation on the results obtainable from the experimental setup. For most optical pumping system the sample gas is in a chamber which has two mirrors rather than windows. The first mirror allows the laser beam to enter the chamber but is a total reflector on the inside of the chamber. The second mirror is a partial reflector which will permit only a portion of the laser beam to leave the chamber. The other portion of the beam is reflected back through the chamber. This combination of mirrors causes a percentage of the laser beam to pass back and forth through the sample many times. There is a greater probability that a sample molecule will absorb a photon of laser energy with each additional pass of the beam through the cell. These mirrors are usually germanium and are expensive. CsBr windows were used on our sample cell for economic reasons.

Now that the limitations of the experimental system are known, attention will be directed to remedies for the problems. First and foremost is the need for a more sensitive detection method. As mentioned, the Infrared Spectrophotometer had neither the frequency nor the low pressure capabilities needed for the detection of decomposition of gases under normal optical pumping conditions. Other detector alternatives include the use of gas chromatography. While the gas chromatogram does not solve all of the problems encountered with

IR use, it does eliminate the frequency range problem. There are, however, difficulties foreseeable with the gas chromatography system. Identical retention times for two or more compounds will result in difficult analysis of the spectra. Also, gas chromatography suffers from the same pressure limitations as the IR detection method. Because of these shortcomings it is not suggested that gas chromatography be the sole method of detection. Rather, using it in conjunction with another type of detector which is capable of eliminating the gas chromatography limitations might provide satisfactory results.

The most promising type of detector for these experiments is a mass spectrometer. This method of analysis uses extremely low pressures, lower than those required for laser work. The mass spectrometer also covers a wide range of mass to charge numbers. The detection capabilities would only be limited for samples of large molecular weight, with the upper limit dependent on the individual instrument. Decomposition of a gas would result in different concentrations of molecules at the various mass to charge numbers. At a low attenuation changes in relative peak heights should be easily identified. The mass spectrometer would also give an indication of what the products of the decomposition were.

A second improvement in the experimental system would be to use a different type of sample cell. As mentioned previously, a chamber outfitted with mirrors rather than

windows would provide closer experimental agreement with normal optical pumping conditions.

Finally, as brought out in the discussion of decomposition of gases already studied in published literature, the normal optical pumping conditions include a high powered laser or flash photolysis. Often a pulsed laser was used as the pump. The pulsed laser provides a laser beam of short duration but of very high power. The gases being pumped have a greater probability of absorbing enough energy to break bonds when the energy input is large. The model C250 Molelectron laser is limited to a maximum output of approximately 22W on the strongest of CO_2 bands. Many of the literature references list experimental laser powers of 200 to 3000W. Therefore, a more powerful laser would improve the experimental setup.

Of the possible changes needed to be made in the experimental setup, the only one feasible with the time and money available was the introduction of a mass spectrometer as the detector.

MASS SPECTROMETER INTRODUCTION

The principles behind mass spectroscopy are relatively simple. A compound is bombarded with an electron beam which causes the compound to break up into fragments. The positive ion fragments are then accelerated to a detector. A spectrum is obtained of the number of fragments of each mass to charge ratio. Identification of the compound is then possible through the fragmentation pattern and identification of the parent peak. The instrumentation required to make all this occur is highly complex and expensive.

The following discussion of the mass spectrometer is designed to coincide with the Consolidated Electrodynamic Corporation instrument used in this research and is not meant to describe the general case. The first component part is the sample handling system. This system must allow for the introduction of a low pressure sample into the main body of the instrument. There must also be a method for determining the sample pressure. The CEC instrument uses a glass inlet system. This apparatus provides a small area for original sample introduction. The sample is then expanded into a large bulb and the pressure reading can be obtained from a micromanometer.

The sample passes from the expansion bulb through a molecular leak into an ionization chamber which operates at 10^{-5} to 10^{-6} torr. At this point the sample is hit at a right angle with an electron beam from a heated filament, in this case a tungsten filament. The positive ion fragments

are accelerated through the various slits shown in Figure 10 by means of an accelerating voltage. After the fragments are accelerated, they are sent into the analyzer tube. Only those fragments with the proper velocity make it through the tube to the collector. The velocity is a function of the mass to charge ratio and the accelerating voltage. All fragments of velocities other than the one desired are lost as they hit the tube walls. Therefore, to obtain a spectrum the accelerating voltage is varied. The fragments which are of the proper velocity hit the collector, where the signal is amplified and passed on to the recorder.

The simplest fragment which can occur is the removal of a single electron from the sample molecule to form a molecular ion. This ion will give the exact weight to the nearest whole number of the molecule, rather than an average weight of the isotopes. This peak is also the peak with the highest molecular weight with two exceptions. The first exception is that of molecules containing isotopes which will result in a $M+1$ or $M+2$ (M being the molecular ion) peak. There are also ion fragment - molecular ion collisions which will cause a peak at a higher mass to charge ratio. At normal pressures hydrogen transfer is the major collision process and will lead to an enhancement of the $M+1$ peak which is pressure dependent.

Identification of compounds is based on the principle that peak heights are proportional to the number of ions

at each mass to charge ratio. The molecular ion need not be the largest peak. If the compound is easily fragmented at one particular spot, a fragment peak may be the largest. The largest peak is denoted as the base peak.

The quality of the mass spectrometer is determined by its resolution (R)

$$(9) \quad R = \frac{M}{\Delta M}$$

where M is the higher mass to charge number of two peaks and ΔM is the difference between the two mass to charge numbers. For our purposes a resolution of approximately 250 is desirable. This will give peak separation for all whole mass to charge numbers up to 250.^{45,46,47}

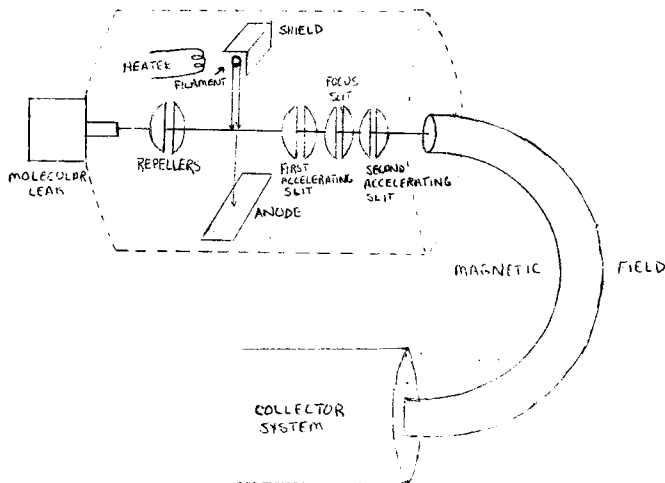


FIGURE 10
CYCLOID TUBE

EXPERIMENTAL PROCEDURES

SAMPLE INTRODUCTION FOR THE MASS SPECTROMETER

Components:

Consolidated Electrodynamics Corporation Mass Spectrometer
Fisher Recordall Series 5000
Glass Inlet System

The glass inlet system used in conjunction with the CEC Mass Spectrometer is diagramed in Figure 11. During initial pump down stopcocks 1 and 8 must be closed and all others must be open. 1 and 8 are open to the atmosphere and if left in the open position will not allow vacuum to be established. The pump down procedure for the entire instrument and method for turning on the cycloid tube filament are given in the Consolidated Electrodynamics Corp. Mass Spectrometer handbook.

Before any samples are used in the instrument a background spectrum must be run. A chart speed of 1 inch per minute and an attenuation of 100 proved to give the most satisfactory results. The background spectrum appears in the mass to charge range of 12 to 40 or voltage range of 110 to 38 v.

The sample cell is now attached to the 12/30 ground glass fitting above stopcock 1. An adaptor which has a 12/30 fitting at one end and a 19/38 fitting on the other must be used to make this connection. Stopcocks 2 and 5 must be closed to isolate the sample inlet area from the cycloid tube area. Stopcock 1 is opened which results in the evacuation of the area between stopcock 1 and the sample cell. After five minutes close stopcocks 3 and 4 and open

stopcock 2. Now open the stopcock on the sample cell until the desired sample pressure is put into the system and reclose the sample cell stopcock. The sample pressure can be read off the mercury column. Stopcock 2 is closed to isolate a portion of the sample in the 3 ml section of the inlet system between stopcocks 2 and 3. The sample is now introduced into the expansion bulb and cycloid tube by opening stopcock 3. This is approximately a 1000 fold expansion.

Allow three minutes for the sample to enter the cycloid tube through stopcock 6. The sample spectrum is now ready to be run. A chart speed of 1 inch per minute has proven effective for mass to charge numbers 12 to 60 or voltages 115 to 27 v. At mass to charge number 60 the peaks are becoming too closely spaced to permit individual identification. Therefore, a chart speed of 2 inches per minute should then be used. The attenuation setting which provides the best results will be determined by the pressure of the sample in the system.

Stopcocks 2, 4, and 5 should now be opened and stopcock 1 closed. This allows the inlet system to be evacuated of the sample. Disconnect the sample cell from the adaptor. The sample should now be subjected to twenty minutes of irradiation from the laser. After the lasing is complete a second spectrum of the sample must be taken using the procedure outlined above. It will be virtually impossible to get the same pressure into the inlet system as was obtained on the first run. Decomposition analysis should

therefore concentrate on changes in relative peak heights from initial spectrum to final spectrum.

Some of the maintenance procedures for the mass spectrum not given in the CEC handbook are included in the appendix.

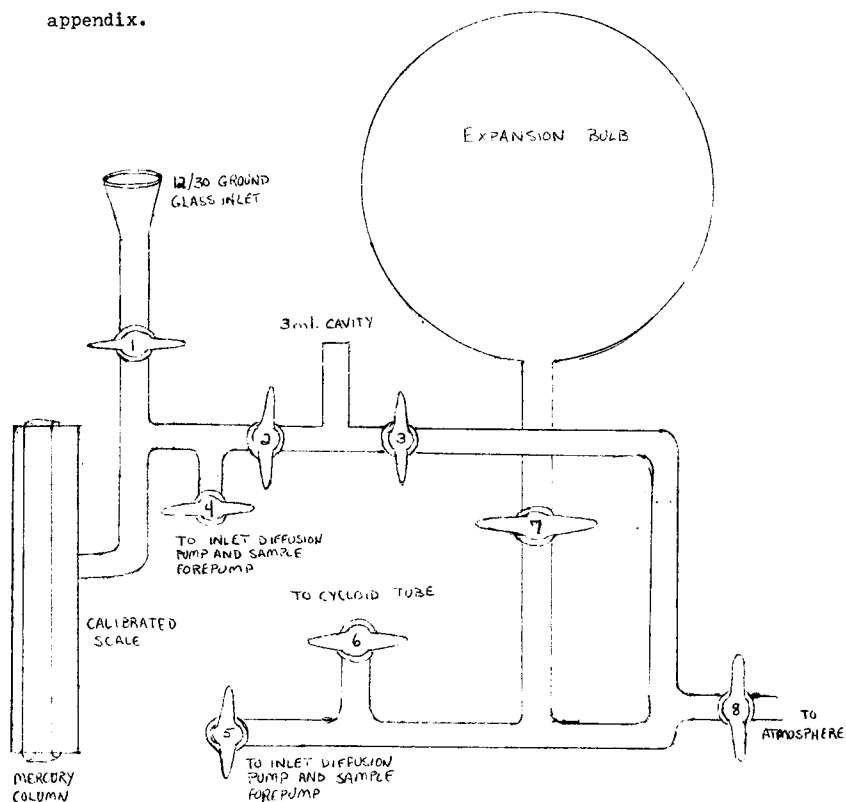


FIGURE 11
GLASS INLET SYSTEM

RESULTS

The mass spectrometer used for this research had not been in operation for at least two years. The instrument itself dates back approximately twenty years. After an overhaul and cleaning, the first step was to obtain a background spectrum. It was known that the mass to charge ratios varied inversely with the accelerating voltage in an exponential manner. However, there was no knowledge of what specific mass to charge numbers would appear at the voltages. The first usable background spectrum was obtained using an attenuation of 100 and a chart speed of 1 inch per minute. Peaks were seen at various voltages between 128 and 36 v.

Several assumptions as to what these peaks represented were made. The major difficulty was the inability to fit the spectrum to the expected 4:1 ratio of N_2 to O_2 . A second background spectrum was run at an attenuation of 1 and provided several more small peaks which had not been detected at the larger attenuation. A spectrum was then taken with an O_2 spike added to the system. Peaks at 49 and 96 v increased over background levels and were assigned mass to charge numbers of 32 and 16 respectively. This spike also clarified the 4:1 ratio problem. The background O_2 peak was small indicating the existence of a good vacuum. The peak corresponding to the 28 mass to charge number was probably comprised of N_2 , CO, and C_2H_4 fragments, causing a larger than originally expected peak. The carbon fragments have been attributed to Octoil vapors from the diffusion pump.

For confirmation of these new assumptions an N_2 spike was performed. As expected the peak at 56 v increased over background levels, as did the peak at 110 v. These two peaks were assigned mass to charge numbers of 28 and 14 respectively.

A second look was taken at the background spectrum run at an attenuation of 1. Because of the unit resolution, mass to charge numbers of 12 through 20 and 25 through 32 were tentatively identified, with 14, 16, 28, and 32 known.

Having a beginning knowledge of the correlation between mass to charge numbers and voltages, a cyclohexane sample was introduced into the system. Cyclohexane's peaks were listed in the CEC handbook, with peak heights all relative to the base peak.⁴⁸ The parent peak of C_6H_{12} was assigned a mass to charge number of 84 at a voltage of 20 v. The following mass to charge numbers were also identified along with the probable fragments causing the peaks: 83, C_6H_{11} ; 70, C_5H_{10} ; 69, C_5H_9 ; 68, C_5H_8 ; 67, C_5H_7 ; 57, C_4H_9 ; 56, C_4H_8 ; 55, C_4H_7 ; 54, C_4H_6 ; 53, C_4H_5 ; 52, C_4H_4 ; 42, C_3H_6 ; 41, C_3H_5 ; 40, C_3H_4 ; 39, C_3H_3 .

Another background spectrum was run at an attenuation of 1. With the additional peaks now identified, mass to charge numbers of 32 through 45 were tentatively identified. Both this spectrum and the cyclohexane spectrum destroyed one of the previous assumptions. It had been assumed that a relatively large peak at 40 v was the result of CO_2 fragments which would be assigned a mass to charge number of 44.

However, these last two spectra indicated that this peak should be a mass to charge number of 40. In order to clarify the situation, an Argon spike was run. The results showed that the peak at 40 v was indeed mass to charge number 40. The next step was to determine where the CO_2 (m/e 44) peak was. A CO_2 spike was run and mass to charge number 44 was assigned to voltage 36.

Enough mass to charge numbers had been identified to allow a plot of time vs $\ln(\text{voltage})$ to be drawn. The plot resulted in a straight line and the equation of the line was calculated (see Graph 1)

$$(10) \quad \ln(v) = -.113(t) + 5.05$$

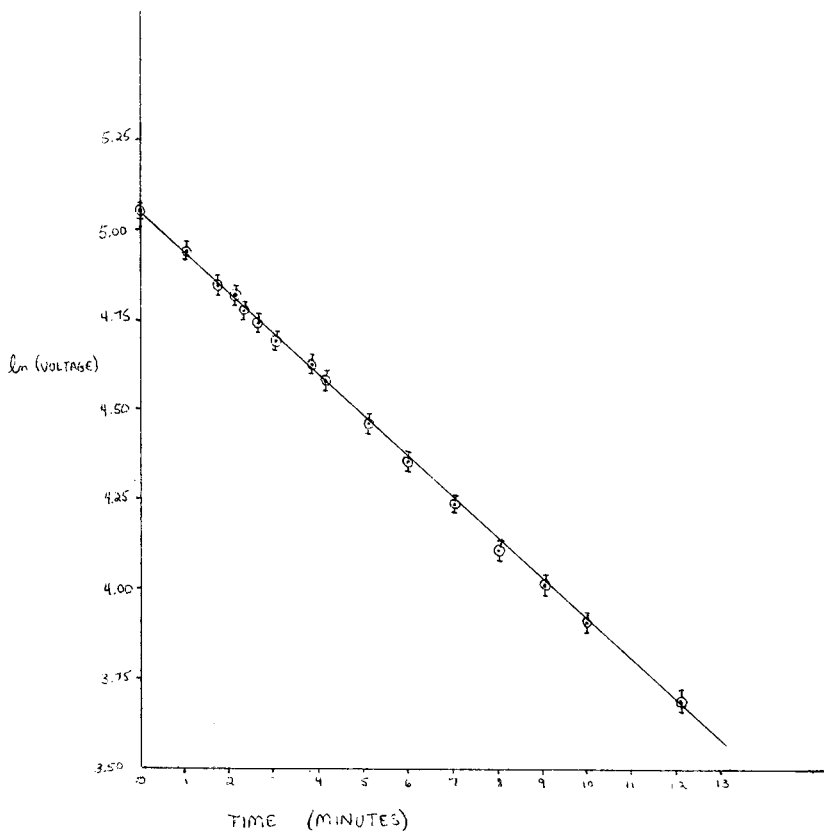
By obtaining the chart speed and starting voltage, the voltage correlating to a mass to charge number could now be calculated. This calculation was more accurate than the readings obtained from the voltage meter. Using a different starting voltage merely alters the y intercept of the line.

Freon 13 (CF_3Cl) was the next sample used for mass to charge number identification. The following mass to charge numbers were identified: 87, $\text{CF}_2\text{Cl}^{37}$; 85, $\text{CF}_2\text{Cl}^{35}$; 68, CFCl^{37} ; 66, CFCl^{35} ; 50, CF_2 ; 49, CCl^{37} ; 47, CCl^{35} ; 37, Cl^{37} ; 35, Cl^{35} ; 31, CF. The isotope effects of Cl were clearly seen, especially at the mass to charge numbers 35 and 37.

$\text{CF}_2=\text{CClF}$ was also run in the mass spectrometer and provided identification of the following: 118, $\text{CF}_2=\text{CCl}^{37}\text{F}$; 116, $\text{CF}_2=\text{CCl}^{35}\text{F}$; 99, $\text{CF}=\text{CCl}^{37}\text{F}$ or $\text{CF}_2=\text{CCl}^{37}$; 97, $\text{CF}=\text{CCl}^{35}\text{F}$ or

GRAPH 1

\ln (VOLTAGE) VS time
FOR MASS SPECTRUM PEAKS



$\text{CF}_2=\text{CCl}^{35}$; 87, $\text{CF}_2\text{Cl}^{37}$; 85, $\text{CF}_2\text{Cl}^{35}$; 68, CFCI^{37} ; 66, CFCI^{35} ; 50, CF_2 .

All the mass to charge numbers identified through these sample materials, along with some which were extrapolated, are listed in Table 5. The time values are a measurement from the various spectra and are based on the chart speed. The voltage values are obtained by calculation using equation 10.

TABLE 5
IDENTIFIED MASS TO CHARGE NUMBERS

MASS	TIME* (min)	VOLTAGE**	MASS	TIME* (min)	VOLTAGE**
13	2.66	115.5	50	13.93	32.3
14	3.06	110.4	51	14.10	31.7
15	3.64	103.4	52	14.28	31.1
16	4.18	97.3	53	14.43	30.6
17	4.70	91.7	54	14.59	30.0
18	5.16	87.1	55	14.74	29.5
19	5.52	83.6	56	14.90	29.0
20	6.06	78.7	57	15.04	28.5
24	7.65	65.7	62	15.76	26.3
26	8.31	61.0	63	15.89	25.9
27	8.66	58.6	64	16.02	25.5
28	9.00	56.4	65	16.15	25.1
29	9.24	54.9	66	16.27	24.8
30	9.59	52.8	67	16.39	24.5
31	9.90	51.0	68	16.52	24.1
32	10.10	49.8	69	16.64	23.8
33	10.35	48.4	70	16.76	23.5
34	10.59	47.1	71	16.88	23.2
35	10.85	45.8	81	17.98	20.4
36	11.10	44.5	82	18.08	20.2
37	11.35	43.3	83	18.17	20.0
38	11.62	42.0	84	18.28	19.8
39	11.86	40.8	85	18.39	19.5
40	12.06	39.9	86	18.50	19.3
41	12.29	38.9	87	18.61	19.1
42	12.50	38.0	97	19.51	17.2
43	12.69	37.2	99	19.70	16.9
44	12.89	36.4	101	19.93	16.4
45	13.06	35.7	103	20.10	16.1
46	13.25	35.0	104	20.17	16.0
47	13.41	34.3	116	21.06	14.4
48	13.59	33.6	112	21.20	14.2
49	13.75	33.0			

*The time is based on a starting voltage of 156 v. Each value has a ± 0.03 error

**Each voltage value has a ± 0.1 error

CONCLUSIONS

The calibration results obtained from the mass spectrometer indicate that the use of this instrument in place of the infrared spectrophotometer would be a major improvement in the gas decomposition experimental setup. The low pressures used by the mass spectrometer matches well with normal laser pumping conditions. The wide mass range of detection allows for analysis of all gases of interest in this study. The effect of elevated temperatures due to absorption of radiation by the sample would be minimized allowing for greater accuracy in peak height comparisons between initial and final spectra.

Continued work is warranted in the study of gas decomposition due to laser stimulation. Using the mass spectrometer as the detection system, the survey of gases known to emit radiation when subjected to laser stimulation should be completed. This work should be done at pressures in the mtorr to 5 torr range. Also, where a gas is known to emit radiation when hit with each of several different laser lines, each of these lines should be tested concerning whether or not decomposition of the gas occurs upon stimulation.

APPENDIX A

SAMPLE DIFFUSION PUMP OIL CHANGE

- 1) The sample diffusion pump is located at the bottom of the bakeout column in the right hand side of the cabinet.
- 2) The exhaust forepump should be off. The shut off valve should be open, while the vent valve, bypass valve and isolation valve should be closed.
- 3) Using a mirror as a sight aid, remove the nut which holds the heating plate in place.
- 4) Move the rust colored heating plate out from underneath the column without disconnecting the attached wires.
- 5) Place a petri dish or similar receptacle underneath the Allen screw.
- 6) Remove the Allen screw and let the oil drain.
- 7) Put approximately 70 ml of Octoil in a clean petri dish.
- 8) Connect a short section of tubing (approximately 4 inches long) to the protruding connection on the pump.
- 9) Turn on the exhaust forepump and place the free end of the tubing in the new Octoil.
- 10) After almost all of the oil has been sucked into the pump, replace the Allen screw and tighten one or two turns. Immediately shut off the exhaust forepump (continued operation of the exhaust forepump will draw Octoil vapors into the forepump).
- 11) Tighten the Allen screw, reposition the heating plate and tightened the nut.

APPENDIX B

INLET DIFFUSION PUMP OIL CHANGE

- 1) The inlet diffusion pump is located behind the glass inlet system partition.
- 2) The sample forepump should be off. The two stopcocks in the glass inlet system which open the inlet system to the diffusion pump should be closed.
- 3) Remove the nut which holds the heating plate in place. This is most easily done by working from the back of the instrument with the power drawer pulled out.
- 4) Move the heating plate from underneath the pump without disconnecting the wires.
- 5) Loosen the Allen screw in the bottom of the pump.
- 6) Either hold or position a petri dish beneath the Allen screw. Remove the Allen screw and let the oil drain.
- 7) Put approximately 40 ml of Octoil in a clean petri dish.
- 8) Connect a short section of tubing to the protruding connection on the pump.
- 9) Turn on the sample forepump and place the free end of the tubing in the new Octoil.
- 10) After virtually all of the oil has been sucked into the pump, replace the Allen screw and tighten it one or two turns. Immediately shut off the sample forepump.
- 11) Tighten the Allen screw, reposition the heating plate and tighten the heating plate nut.

APPENDIX C

CHANGING OF MECHANICAL PUMP OIL

- 1) Unplug both pumps. The plugs are located in the back left corner of the cabinet
- 2) Disconnect all hoses from the pumps and lift the pumps out of the cabinet
- 3) Place an oil pan beneath the screw cap located on the side of the oil section of each pump.
- 4) Remove the screw cap and let the pumps drain. Check the belts for signs of wear and lubricate the motors with a light oil.
- 5) Replace the screw cap and fill the pumps with Duo Seal vacuum pump oil to the level indicated in the small window on the oil section of the pump.
- 6) Place the pumps back in the cabinet, connect the hoses and plug the pumps in.

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