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CALIFORNIA UNIV SANTA BARBARA DEPT OF CHEMISTRY

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THE EFFECT OF PRESSURE AND TEMPERATURE ON LUMINESCENT PROCESSES--ETC(U)

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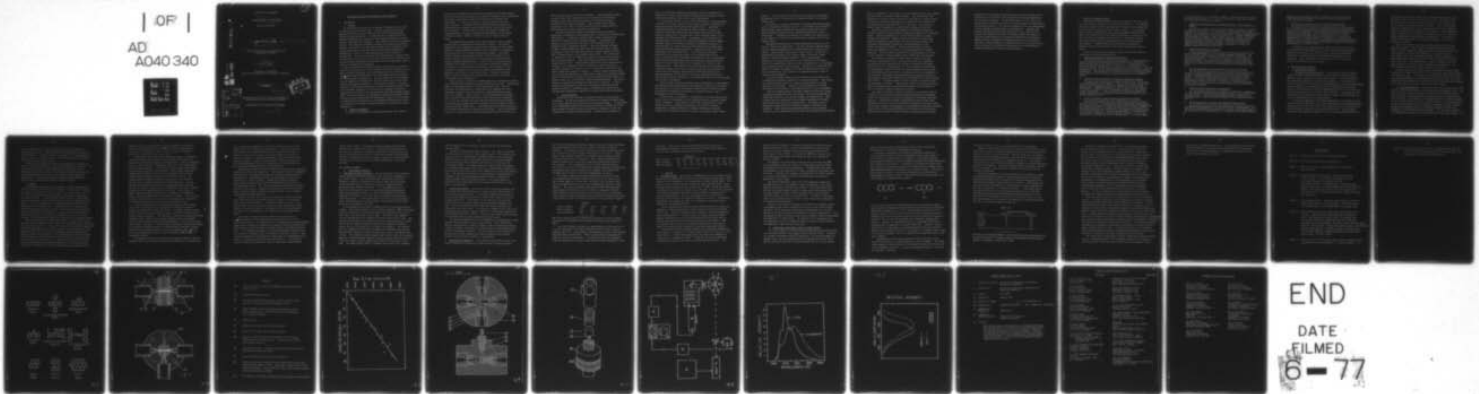
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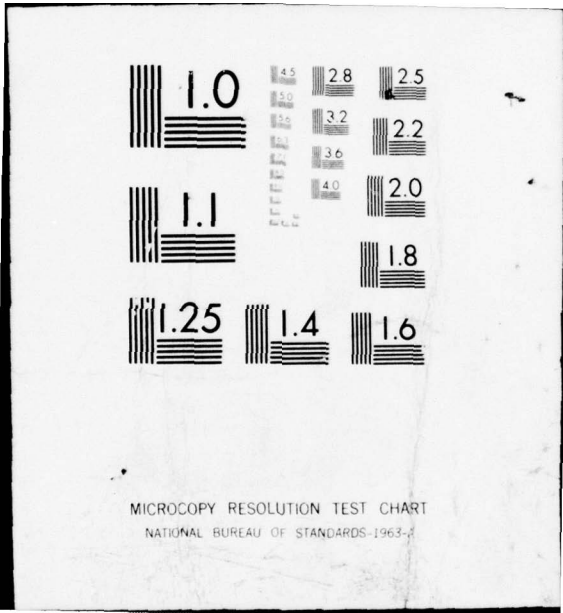
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(6) The Effect of Pressure and Temperature on Luminescent Processes

by

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ELECTRONIC PROPERTIES OF MATERIALS AT HIGH PRESSURES

I. INTRODUCTION

A. General

At the present time interest and activity in high-pressure research are growing at an accelerated rate. Thus our knowledge of the bulk properties of matter has been extended to pressures exceeding several hundred thousand atmospheres. By contrast, our information about the electronic properties of materials is still largely confined to a narrow pressure range about one atmosphere. This disparity arose for experimental reasons: the single most important technique for studying the electronic properties of materials has been optical spectroscopy, and optical cells require transparency, while high-pressure cells require strength and malleability - which are usually associated with the antithesis of transparency. Thus the two disciplines of spectroscopy and high-pressure research had to be successfully wed, before the electronic properties could be measured and correlated at high pressures and this information could be useful in technological applications.

→ The characterization of ^{these} ~~these~~ properties which depend on electronic processes in materials under high mechanical stresses is important to many areas of modern technology, since sophisticated electronic devices and specialized materials applications are increasingly required to function in extreme pressure environments. For this purpose the basic knowledge must be assembled to determine the electronic properties of matter under extreme environmental conditions. The molecular energetics of various materials in environments which differ from the isothermal, isobaric world of our everyday experience is the theme of this report, covering work sponsored by the Office of Naval Research from April 1971 through December 1974. → This work combines the experimental techniques of condensed state research, optical spectroscopy and high-pressure research for the purpose of using the pressure parameter in understanding compressed matter and as a perturbation to elucidate electronic properties of materials at normal pressures.

B. Pressure Techniques

The dearth of information on electronic properties under pressure

despite man's fascination with the pressure parameter was directly related to the slow evolution of apparatus and techniques available to the experimenter. Even today is high-pressure optical work confined to relatively few laboratories. In the present report we will be concerned only with static pressures. The upper limits of attainable static pressures are determined by the strength of the materials and the construction design of the apparatus. The development of new strong alloys coupled with ingenious designs have made it possible to reach pressures of the order of 400 kbar (1 kbar = 987 atm = 14,504 psi) in very small volumes of matter.

The apparatus for achieving static high pressures requires suitable construction to withstand great compression or tension. The optical high-pressure cell adopted in this laboratory is modeled after the common design of a piston-cylinder combination in which pressure is developed by forcing a piston into a cylinder containing the sample. The piston material demands a high crushing strength, while the material of the cylinder must possess sufficient tensile strength to withstand several percent elongation without rupture. A wide variety of alloys and heat treatments exist today to give a wide spectrum of mechanical properties. In addition to the proper choice of materials, special methods of construction are crucial and the success or failure of an apparatus often depends on the details of a particular design. Moreover, the proper choice of these fine details are usually discovered only by trial and error rather than by calculation.

Pressures below ~ 50 kbar are commonly produced by intrusion of a piston into a cylinder and transmitted by another medium to the sample. At pressures below the solidification point a fluid medium may be used. Here the difficulty of avoiding leaks is compensated by the attainment of truly hydrostatic pressures, possible only with a transmitting medium having zero shear strength. Above ~ 20 kbar, only quasi-hydrostatic pressures can be achieved since most materials are then solids at room temperature. It is clear that internal friction within the solid and surface friction between the moving components of the apparatus cause some departure from a purely hydrostatic stress field. The measurement of the sample pressure is an additional complication at pressures above 10 kbar. Below ~ 10 kbar the pressure on a fluid can be accurately measured from the force exerted on a

free (rotating) piston of known cross-section. Such measurements define a pressure scale which can then be used to calibrate less cumbersome secondary gauges whose operation depends on the sensitive pressure dependence of some physical property. This secondary gauge extends the pressure scale above ~ 10 kbar and may be used to assign values to fixed points such as phase transitions in materials.

The above discussion outlines some problem areas about pressure generation, transmission and measurement which is shared by all high-pressure experimenters. In addition, optical studies require a provision for radiation to enter and leave the sample chamber. To withstand the pressure an optical cell can have only a small fraction of its area composed of weak, transparent material. The first attempts by Amagat in 1887 to employ windows were made with small truncated cones of glass enveloped by a layer of ivory which served as a gasket between the glass and its tapered socket in the supporting steel block. The windows were so tapered that they were driven more tightly into their conical sockets with increasing pressure. These glass windows consistently withstood compression to 1 kbar. Poulter greatly advanced the art of window design by using a short cylindrical block of transparent material (quartz or sapphire) supported on a steel base over an entire face except for a small hole to admit light through the support. A Poulter window of proper thickness and properly supported by a mating steel surface has a practical working limit of ~ 12 kbar and is widely used to obtain optical data on highly compressed fluids, and on solids with a fluid transmitting medium. New window designs are required for working with solids above ~ 10 kbar. As far as windows in piston-cylinder vessels are concerned, designs based on the apparatus reported by Drickamer, et al., in 1957, are most successful in achieving quasi-hydrostatic pressures, the present work being no exception.

C. Pressure Effects

Recent years have witnessed a tremendous increase in high pressure technology. The pressure parameter has become an extremely versatile tool for the investigation of a wide variety of physical phenomena. Its importance as an experimental variable arises from the fact that it affords one of the most convenient methods to modify the molecular environment or alter the intermolecular distance between molecules. Modern physical theories of

matter are based upon molecular interactions, and only recently has the combination of optical spectroscopy and high-pressure technology received significant attention in the study of these interactions.

Of particular interest is the effect of high pressure on the electronic transitions of organic molecules and the various processes responsible for energy dissipation from electronically excited states. Apart from accompanying changes in the solvent or matrix density, viscosity, or refractive index upon compression, high pressure may perturb the intramolecular energy levels of the molecule, thereby inducing changes in its absorption and emission spectrum. In addition, the distortion of the electron cloud by the presence of dipolar or multipolar electric moments, resulting simply by the greater proximity of neighboring molecules at high pressures, may excite rotational and vibrational transitions which are normally inactive spectroscopically - thereby resulting in a diffuse broadening of the vibrational bands. Such changes are generally manifested in the luminescence properties of complex molecules and provide useful and direct information concerning the role of environmental perturbations on the processes involved in electronic relaxation and the nature of the interaction forces between molecules as a result of the applied pressure. High pressure optical spectroscopy therefore provides a prominent method in the study of electronic structure and the nature of excited state interactions, providing the accompanying changes in the physical properties of the solvent or matrix are understood relative to those changes which are reflected in the luminescence behavior of the molecular system under investigation.

Of the numerous techniques employed in the investigation of environmental perturbations, high pressure optical spectroscopy is perhaps the most recent. The versatility of the pressure parameter arises from its ability to modify the molecular environment in the absence of secondary factors, such as temperature or solvent variation.

Listed in Fig. 1 are examples of the structures of several organic molecules, which are representative of the particular class of compounds studied in this laboratory. They have been used in the investigation of a wide variety of processes commonly encountered in the study of electronic spectroscopy, including intersystem crossing, conformational disorder, excited-state interactions, two-level emission, and singlet-singlet energy

transfer. For this reason, they reflect some of the more interesting implications derived from high-pressure optical studies of the excited singlet state.

The crystals of aromatic hydrocarbons are weakly interacting systems both in structural and electronic terms. Van der Waals forces (induced dipole-induced dipole interactions) are primarily responsible for the observed binding energy, while H-H repulsions determine the crystal orientations. Electronic interactions are likewise quite small, being on the order of 1 to 10 cm^{-1} for triplet states, and 10 to 10^3 cm^{-1} for singlet states.

Two major characteristics of aromatic hydrocarbon crystals are the result of these weak interactions. The weak electronic coupling implies that the spectral properties of a molecule measured for example in the crystal will be little altered by the crystal field. Because kT is appreciable with respect to the binding energy, one expects a large degree of thermally activated disorder. Since energy transfer properties of a crystal are related to the equivalency of the lattice sites it is apparent that defects can play an important role in determining the electronic processes in the crystal. Although it is established that defects in general are important in affecting electronic processes, as well as conductivity, mass diffusion, and chemical reaction, little is known of their properties.

The aim of crystal studies at high pressures was to determine the structural and electronic properties of a particular defect. This defect, the "excimer-forming" defect, is created by application of very high pressures to the crystal. Studies of defect properties are greatly facilitated by the ability to vary sample pressure as well as temperature.

The most commonly measured electronic properties include the energy, intensity, and polarization of a transition; the spectral bandwidth and vibrational structure; the emission lifetime and quantum yield. Many articles have been written about the electronic properties of aromatic hydrocarbons which will not be repeated here. The optical study of compressed crystals focused on transition energies, bandwidths, and lifetimes. Their values are determined primarily by the electronic structure of the isolated molecule, but they can be modified by interactions

with the environment. The energy levels of isolated molecules are replaced by energy bands in crystals, called excitons. The long lifetime and pathlength of triplet excitons suggests the possibility of exciton-exciton interactions, leading to quenching to the ground state and promotion to the singlet state, respectively [$T_1 + T_1 \rightarrow S_0 + S_1$]. This process of triplet-triplet annihilation is referred to as delayed fluorescence.

Imperfect crystals are characterized by local disorder which can seriously influence energy migration, leading to trapping of the electronic energy. Chemical impurities, as well as physical defects, provide a mechanism for trapping. Studies of the role of defects in quenching exciton migration are complicated by the fact that the structure, concentration, distribution, temperature, and time dependence of the defects are generally unknown. Pressure-induced defects provide an interesting approach to the study of electronic properties of organic materials. Pressure studies contribute to an understanding of the role of these defects in energy trapping, both in single and mixed crystals.

In conclusion, techniques of high pressure research, molecular electronic spectroscopy and the solid and fluid state are combined for measuring electronic processes under unusual environmental conditions. The influence of the environment on the several energy dissipation paths of electronically excited molecules have been characterized and used for the understanding of matrix effects at various pressures and temperatures. The absorption, fluorescence and phosphorescence of organic molecules in solid matrices and liquid solutions have been studied in the range 0-40 kbar and 77-400°K. One prime parameter of great interest in physical science and technology is distance. High pressure studies are uniquely suited for gaining information about intermolecular distances and the influence of their variations on physical properties of solids.

The study of electronic structure of molecules in condensed media as a function of pressure gives useful information regarding environmental effects on energy levels, transition probabilities, and energy relaxation processes. Electronic absorption spectroscopy at high pressures gives information about the solvation of molecules in different electronic states, the selective response of chromophores to environmental compression, molecular conformation, and the compressibility of weak chemical bonds such as are formed between molecules in charge-transfer or hydrogen-bonded complexes.

Luminescence spectroscopy at high pressure measures the influence of the environment on the radiative and radiationless transition probabilities for electronic relaxation. Of particular interest is the role of the medium in such radiationless processes as various types of energy transfer and chemical quenching. The pressure parameter adds to our understanding of most problems in photochemistry and photophysics. Although high-pressure perturbation (0-40 kbar) represents a novel method for the study of the electronic structure of materials, nearly all methods of electronic spectroscopy can be adapted and modified for high pressure optical studies, including the simultaneous variation of temperature. The Office of Naval Research has supported this work in the past several years to develop the techniques and apply them to an understanding of electronic processes in solid and liquid materials.

D. Summary of Technical Reports

Two graduate students earned their Ph.D. during this time span, while two others have not completed their dissertation research. The financial support from ONR has been deeply appreciated and has been most significant in supporting the graduate research of these students. In the period April 1, 1971 to December 1974, four contracts (N00014-69-A-0200-8010, Mod 01, 02, and 03) in the total amount of \$105,400 were written for the task "the effect of pressure and temperature on luminescent processes (the organic solid state) and luminescent probes in extreme pressure environments". Fourteen quarterly status reports delineated our progress (successes and failures) in the various high pressure optical studies.

In this time period, nine technical reports were written which are reproduced by title and abstract below:

1. Excimer Fluorescence of Poly(N-vinylcarbazole)

Fluorescence spectra and lifetimes of carbazole, 1,3-bis(N-carbazolyl)propane and poly(N-vinylcarbazole) have been studied as a function of pressure to 30 kbar at room temperature and 77°K. Polymer films show exclusively excimer fluorescence ($\tau = 43$ nsec) at room temperature. This is not quenched at 77°K but appears together with a new emission ($\tau = 12$ nsec) attributed to traps arising from exciton coupling between adjacent carbazole chromophores. The comparative P, T response of the three compounds suggests that excimers do not form between adjacent chromophores in the amorphous polymer.

2. Excimer Delayed Fluorescence of Compressed Naphthalene Crystals

The compression of naphthalene crystals (to 30 kbar) at 77°K creates, irreversibly, defects in the lattice. These defects capture singlet and triplet excitons, leading exclusively to excimer and delayed excimer fluorescence. Triplet trap depths of ~ 600 cm⁻¹ at 1 atm and ~ 700 cm⁻¹ at 30 kbar are estimated from the temperature dependence of the delayed excimer fluorescence. A wide distribution of singlet trap depths and excimer conformations is indicated by the pressure modifications of the excimer fluorescence band.

3. Effect of Pressure on Pyrene Excimer Fluorescence in Toluene

The pressure dependence of pyrene fluorescence in toluene has been measured to 10 kbar. The monomer and excimer fluorescence decay kinetics are analyzed to give the rate parameters for excimer formation, dissociation, and unimolecular decay as a function of pressure at 296, 320, and 340°K. Activation parameters are evaluated both as a function of temperature and as a function of pressure. The pressure dependence of the association is in one-to-one correspondence with the solvent viscosity. The rate of dissociation is strongly inhibited by high pressures. The volume change

on excimer formation is $-11 \text{ cm}^3/\text{mole}$ at 296°K . The enthalpy and free energy of excimer formation are -9.7 and -4.2 kcal/mole at 1 atm, and -3.6 and -6.7 kcal/mole at 10 kbar, respectively.

4. Absorption and Luminescence of Aromatic Molecules at High Pressures - A Review

The effects of high pressure on the spectroscopic properties of aromatic hydrocarbons are reviewed. The topics are: aromatic molecules in inert matrices, the spectral shift in the absorption, fluorescence and phosphorescence spectra, band broadening, intensities and lifetimes. Specific interactions between aromatic molecules at high pressures are also included: absorption and fluorescence of electron-donor-acceptor complexes, excited state reactions in solution, excimers in polymers, absorption, fluorescence and delayed fluorescence of aromatic crystals. The report summarizes the application of high pressure spectroscopic techniques to one class of organic materials in the last five years.

5. Two-Level Fluorescence of Ovalene

Ovalene fluorescence has been studied as a function of pressure (0-30 kbar) in condensed media at room and liquid nitrogen temperatures. The red shift of the α and ρ bands are 8 and $22 \text{ cm}^{-1}/\text{kbar}$, respectively, in polymethylmethacrylate. The fluorescence kinetics are consistent with two-level emission; the greater pressure dependence of the lifetimes compared to the relative intensities being attributed to differential level shifts and its influence on the thermal population of the adjacent singlet level.

6. Pressure Dependence of Energy Transfer from Pyrene to Perylene

The efficiency of singlet-singlet energy transfer between pyrene and perylene in polymethylmethacrylate decreases with increasing pressure, i.e., at 77°K the critical transfer distance R_0 is 44 \AA at 1 atm and 35 \AA at 30 kbar. The factors responsible for the reduced efficiency at high pressure are in order of decreasing importance: the decrease in the fluorescence lifetime of the donor, the increase in the refractive index of the medium, and the decrease in spectral overlap of pyrene fluorescence and perylene absorption.

7. Perylene Excimer Fluorescence in Cyclohexane

The blue monomer fluorescence of perylene in cyclohexane is replaced by an orange excimer fluorescence emission upon freezing the solution with increasing pressure. The temperature dependence of the excimer decay is characterized by a radiative lifetime of 80 nsec and an activation energy of 670 cm^{-1} .

8. Pyrene Fluorescence in Ethanol and Cyclohexane Under Pressure

The fluorescence of pyrene has been studied as a function of pressure, concentration and temperature in the solvents ethanol and cyclohexane. The spectra and lifetime of both monomeric pyrene and the excited state complex are characterized at different pressures. Compression of ethanol shifts the

monomer-excimer equilibrium towards the monomer, while compression of cyclohexane leads to aggregation and pyrene excimer fluorescence over a large concentration range.

9. Naphthalene-d₈ Phosphorescence in Pressure-Perturbed Media

The phosphorescence spectrum and triplet lifetime of naphthalene-d₈ have been measured as a function of pressure (1 atm-35 kbar) at 77°K in five matrices: poly(methylmethacrylate), EPA, perfluoromethylcyclohexane, pentane, and benzophenone. Compression of these matrices results in strong spectral broadening which is attributed to increased solvent inhomogeneity and enhanced coupling with the lattice. The pressure-induced shift in the triplet energy is sensitive to the detailed interactions of host molecules with the solute molecule, and provides qualitative attitudes about the various types of interactions responsible for solvent perturbations of electronic processes.

In conclusion, the technical reports describe the work on solid and liquid materials accomplished during the first half of the contract period. During the latter part, our efforts have been directed towards aqueous environments at high pressures which required the development of new technology. These two thrusts in pressure research are summarized in Section II and Section III, respectively.

II. Solid and Liquid Materials

A. Experimental Techniques

1. The High-Pressure Optical Cell. The successful design for optical studies of solids at pressures above 10 kbar was first formulated by Harry Drickamer and co-workers at the University of Illinois. We have adopted his basic design and applied it to luminescence studies of the compressed state to 30 kbar at temperatures ranging from liquid nitrogen to above room temperatures. This laboratory, as an ongoing process, has been developing and improving apparatus and techniques for studying simultaneously the effects of P and T on the electronic properties of solid and liquid materials. Techniques have been successfully tested to contain samples which are liquid at normal loading conditions (room temperature and one atmosphere).

The critical components of the optical high-pressure cell (Fig.2) are the windows which must withstand a high pressure gradient and retain optical clarity. The window material must also be free from impurities which can interfere with weak luminescence signals from the sample under pressure. Single crystal sodium chloride supported by sapphire ends is the best available material for

transmission of light and pressure to the sample surrounded by the salt. The sample volume is small ($\sim 100 \mu\text{l}$) and therefore the external force required to achieve a sample pressure of 30 kbar is not excessive and can be handled by ordinary hydraulic equipment. Also, a small sample chamber is compatible with a cell weighing only 10 lbs when assembled and measuring about 4" in diameter and 2" in length. These dimensions permit a favorable optical aperture and location of the cell within the sample compartments of many commercial spectrometers. The sapphire windows fail occasionally, but otherwise the optical cell can be used routinely to 30 kbar.

In the use of aqueous solutions with this optical cell, the NaCl presented a problem. This requires an optically transparent plastic which is easily machinable, compressible without shattering and not self-fluorescent (i.e., be free from impurities). The material chosen after lengthy trials was polymethylmethacrylate (PMMA), prepared in our laboratories with mechanical properties which permit optical studies to 10 kbar and above. The PMMA capsule is 0.120" in diameter and 0.150" long, with a press fit cap to prevent leakage under compression. The wall thickness is chosen to minimize rupture and scattering.

To obtain high pressure spectroscopic measurements at liquid nitrogen temperatures, a simple cryostat was used to contain the high pressure optical cell within the press. All components of the dewar are cooled in the press by controlled addition of liquid nitrogen from a transfer tube; the sample temperature being measured by a thermocouple which is inserted into a recessed well of the jacket and situated close to the sample chamber.

2. Pressure Calibration. The pressure within the optical cell has been calibrated by optical detection of phase transitions in inorganic salts. The phase transition of KCl at 19.4 kbar is rather sharp and clearly detected through the sudden reduction in light transmission due to a change from fcc to sc structure. The technique is convenient and simple, but the reliability of the resulting pressure scale was somewhat uncertain. An improved method consists of utilizing the shift of the ruby fluorescence (R_1 line at 6943\AA), accepting the conversion factor of $0.36\text{\AA}/\text{kbar}$ suggested by Barnett and Piermarini at the National Bureau of Standards. The ruby chip is enclosed in ethanol/methanol mixtures or directly with NaCl in the sample chamber. The

pressure-induced shift is shown in Fig.3, which can be converted to a sample pressure scale. These calibrations confirmed earlier methods at room temperature. A further important conclusion is that the hydrostatic nature of the salt medium is better than imagined, because the bandwidth of 6\AA hardly increased below 20 kbar.

There exists no satisfactory method for calibrating the pressure at 77°K , because fixed points are in doubt and the ruby shift is unknown. We suspect that the various methods delineated by Ron Beardslee in his dissertation are valid to $\pm 20\%$. This large error would also include the calibration obtained from the ruby shift (assumed to be temperature-independent). Primary pressure points require acceptance before the pressure scale can be made more precise by optical methods.

B. Results

Spectroscopic measurements as a function of pressure and temperature have been carried out for a number of compounds. Generally, the substance of interest is dispersed in a matrix which is relatively inert; i.e., we are interested in the electronic properties of the chemical impurity in the compressed state. Matrix materials comprise plastics, frozen organic glasses, hydrocarbon liquids, perfluorinated solvents and organic molecular crystals. These materials have the common property that they are bonded primarily by van der Waals forces. Compression of these matrices will reduce intermolecular distances and hence the bonding strength an impurity dispersed in the material experiences as a result of pressure application. The magnitude of these modifications in bonding characteristics at high pressures are reflected in the luminescence response of the embedded impurity.

One basic observation is energy level shifts as a function of pressure. The rate of pressure-induced shifts depend on the characteristics of the matrix material and the impurity. In the case of the matrix the pressure dependence of such bulk properties as the density and index of refraction are of prime importance, while the nature of the electronic transition determines the pressure response of the impurity. The important factors are the strength of the transition, called the f-number, and the relative spacing and number of energy levels in the molecule. The luminescence spectra provide then one means of determining the physical properties of the compressed state. It should be mentioned that theories of intermolecular interactions in the

condensed phase are insufficiently advanced to predict the effects of pressure on electronic transitions and that a number of materials must be surveyed experimentally to discern trends and provide predictive power about new materials under compression.

In addition to the measurement of spectral parameters as a function of pressure insight into pressure-induced effects in materials can be obtained from transient luminescence characteristics. When the excitation source is switched off, the luminescence decays at a rate characteristic of the energy dissipation. For impurities such as aromatic hydrocarbons the decay rates fall into two time ranges; singlet energy states have characteristic lifetimes of the order of nanoseconds (10^{-9} sec) and triplet energy states have lifetimes of the order of seconds. The various processes leading to electronic energy loss, i.e. radiation and heat, may be grouped under electronic relaxation rates. We have observed that electronic relaxation is generally enhanced by pressure and that the pressure coefficient of the logarithmic decay rate is roughly proportional to the compressibility of the matrix. There exists no general theory concerning medium effects on radiative and nonradiative rates, which could predict the observed pressure response. There is again a marked uniformity for a given class of chemical impurities, applicable to electronic relaxation from both singlet and triplet states.

The first-order kinetics for electronic relaxation is only observed under ideal conditions, because frequently other bimolecular processes compete with unimolecular energy dissipation. In plastic matrices, oxygen is able to diffuse into the polymer and quench long-lived excited states of trapped chemical impurities. The diffusion is arrested by increasing pressure, resulting in less quenching and enhanced brightness of the luminescence. Liquid solutions usually contain quenching molecules, so that the long-lived light yield is very small. Such bimolecular quenching is generally eliminated by freezing and cooling the matrix to liquid nitrogen temperature, another method would be to apply pressure to freeze the solution, hence light can be seen from compressed samples at higher temperatures than possible at atmospheric pressure.

The encounter between excited molecule and unexcited molecule (same or different type) in a fluid does not only lead to quenching but can also lead

to new luminescence appearing in a different spectral region from that characterizing the originally excited molecule. Such strong, specific interaction between excited molecules has been well documented for a number of systems, the transient species being called charge-transfer complexes, excimers, or exciplexes (depending on the constituents of the encounter complex). Further, these processes of light conversion are very pressure-dependent because the interaction is a strong function of the intermolecular distance between the two molecules.

High pressure effects on solids generally are not completely reversible, especially far below room temperature. The pressure memory of a luminescent material can be substantial and evident in the optical characteristics of the substance. Irreversible phenomena are particularly evident in the luminescence of organic crystals. Compression introduces physical defects into the lattice which trap the excitation energy and serve as new luminescent centers. This situation can only be corrected by thermal annealing of the crystal, supporting the hypothesis that pressure has produced a thermodynamically unstable situation which can lead to molecular reorientation and light conversion.

Aromatic molecules such as pyrene and perylene in cyclohexane change their luminescent color when passing from the liquid to the crystalline state with increasing pressure. The chemical impurity can serve as an optical probe of phase transitions, either by light conversion or a large change in the light intensity. The explanation is reduced quenching in the solid state or aggregation of the impurity in the crystalline host matrix.

In conclusion, high pressures can modify these processes by a significant amount, thereby controlling the molecular behavior of the luminescent materials. An understanding of the photophysics and photochemistry under extreme environmental conditions may point the direction towards novel applications of organic materials possessing specific technological requirements. The continued development of improved spectroscopic techniques will be fruitful as a diagnostic tool in high-pressure materials research. More detailed information on the theoretical implications and experimental data is found in the technical reports abstracted in Section I. In particular, technical report No. 4 represents a review of high pressure spectroscopic

studies prior to 1972. Many questions remain unanswered and fruitful research areas remain for the future. The interesting applications of the pressure parameter in spectroscopy justify more activity in this new branch of high-pressure research, to learn about structure and electronic processes in molecules dispersed in crystals, polymers or liquid solvents. In addition, the discovery of new phenomena unknown today is entirely possible.

III. AQUEOUS SOLUTIONS

A. Experimental Techniques

1. High Pressure Cell for Liquids. The new direction of our research in aqueous solutions required a new optical cell design that eliminates the use of NaCl windows. The new high pressure optical cell (Fig.4) was designed to enable us to pressurize an aqueous sample and then by means of high pressure valves, separate the cell from a standard pressure generating system (100,000 psi limit). This uncoupling allows us to place the pressurized cell into the spectroscopic monitoring apparatus chosen for a particular study, i.e., Cary 14 spectrophotometer, Perkin-Elmer MPF-3 fluorimeter, or our home-built spectrometers and nanosecond lifetime apparatus. At the present time the cell has been used routinely up to 5,000 atmospheres at room temperature, and has been tested at high pressures at a temperature of 2.0°C.

A conventional type of Poulter-Bridgman design is used for the optical windows. The window material is Linde synthetic sapphires, (60% orientation) 0.250 inches diameter by 0.250 inches length, ground optically flat on both ends with a 0.015 inch radius on both edges. The faces of the sapphires were cut perpendicular to the cylinder axis within 0.001 inch per inch. The sapphires are attached to the lapped faces of the mushroom plugs by a "wring-fit" of the two matched surfaces and then carefully applying an adhesive mixture (G.E. No.7031 varnish) to the edges of the sapphire. The mushroom plugs are supported by thin copper, teflon and brass packing rings that are prevented from extruding by small beryllium-copper rings of triangular cross section. The outermost of these support rings is held in place by a threaded plug with a 10 degree tapered aperture hole and with 3/16 inch deep holes for a four pin wrench so that the plugs can be screwed in flush with the cell body. The sample capsule holder (a stainless steel jacket with a threaded

end) is attached to a fourth plug, a blind version of the other three mushroom plugs.

The pressure transmitting fluid is hexane. The sample is separated from the pressure fluid with a quartz sample capsule. The capsule, shown in Fig.5, has three perpendicular openings to match the cell and permit 90° fluorescence as well as absorption studies of the aqueous solution. The quartz sample capsule dimensions are 0.157 O.D., 0.118 in ID and 0.375 inches length. The sample solution is sealed within this capsule by a tapered teflon piston, which moves as the sample fluid is compressed. Quartz capsules were chosen, since their surface is more inert than metallic ones. The pressure fit between piston and cylinder is controlled by an adjustable screw, thereby avoiding any problems due to mixing of the aqueous solution and the pressurizing fluid. The sample capsule is attached to the mushroom plug and can be removed and inserted as a unit with an extractor tool.

2. Pressure Calibration. The pressure in the liquid high pressure cell is measured with a Heise Bourdon gauge, connected via a 10X de booster to the pressure-generating system. The pressure calibration was similar to the ruby shift calibration described in Section IIA.2 except for the use of YAlO_3 (0.2% Cr^{+3}). This compound is more desirable since it has a larger pressure shift coefficient at room temperature ($0.70\text{\AA}/\text{kbar}$) than ruby. The R line (7228 and 7251 \AA) shifts with pressure determine the calibration curve up to 5 kbar. For example, a reading of 5000 bar on the Heise gauge corresponds to a R line shift of $3.3 \pm 0.2\text{\AA}$, which translates to a sample pressure of 4714 ± 282 bar. Thus, the true sample pressure appears to be somewhat below the value indicated by the Heise gauge.

The pressure calibration was also accomplished by observing phase changes (pressure freezing points) for a few pure liquids. These included the pressure freezing points at 23°C of benzene, carbon tetrachloride, dodecane, n-decane, o-xylene, and dioxane, all of which have been previously measured by other experimental techniques. Of these liquids, carbon tetrachloride, dodecane and n-decane, exhibited sharp and reproducible phase changes, whereas the others were not suitable as fixed points.

3. Nanosecond Time Apparatus. Many lifetime measurements have been made in this laboratory, yet none have involved species in aqueous solution.

R. F. Chen at NIH recently published a paper on the use of Quinine Bisulfate and Pyrene Butyric Acid to be used as lifetime standards for aqueous solutions. The quinine bisulfate solution by means of quenching with NaCl can be adjusted to yield a lifetime from 18.9 nsec to 0.1 nsec. Pyrene butyric acid solutions (using KI as a quencher) can be adjusted to yield a lifetime from 18.0 nsec to 115 nsec. Thus, lifetime measurements of aqueous solutions over a very broad range can be standardized with only two compounds. It is advantageous to use a single reference species which can be varied over many lifetimes by using an appropriate concentration of quenching salt, because relatively few compounds are available with lifetimes above 20 nsec, on which many investigators can agree.

Five sample solutions of quinine bisulfate were made up according to the specifications in Chen's paper that would cover the short end of the lifetime range from 5.0 nsec (this lifetime is near the lower limit of our own apparatus) to 18.9 nsec, by the appropriate addition of sodium chloride. The results obtained by Chen using an ORTEC 9200 nanosecond single photon spectrometer are shown in Table I in comparison with the values obtained in this laboratory using a pulsed N₂ laser in conjunction with an Amperex 56-AVP photomultiplier and a Tektronix Sampling Oscilloscope, as previously described in Technical Report No.8 and illustrated in Fig.6.

Table I

ml of 0.1 M NaCl	0.000	0.217	0.399	0.683	1.73
Chen's τ_F (nsec)	18.9	14.0	11.5	9.0	5.0
This lab τ_F (nsec)	18.7	14.2	12.2	9.0	5.7

The values reported from this laboratory are averages of several lifetime measurements and demonstrate good agreement with those values reported by Chen.

In a similar fashion, solutions of pyrene butyric acid were made up to cover the long end of the lifetime range from 20 to 115 nsec, except the quencher salt is KI. Pyrene butyric acid (Eastman) was twice recrystallized from 70% ethanol and 30% water. Table II shows again the comparison for solutions at the same composition. An inspection of the data indicates only fair agreement of the values noted by Chen and those (averaged) of this

laboratory. Since it is not clear whether Chen's lifetimes were all experimentally verified or only calculated from the Stern-Volmer relation, we cannot draw any further conclusions at this time.

Table II

ml of 0.5 M KI	1.826	1.089	0.721	0.500	0.352	0.246	0.168	0.106	0.057	0.
Chen's τ_F (nsec)	20	30	40	50	60	70	80	90	100	1
This lab τ_F (nsec)	23.7	34.7	41.4	53.2	58.9	69.4	77.6	87.2	94.3	1

B. Results

1. 9-Amino Acridine. Our interest in luminescent species in aqueous environments led us to investigate the effects of a phase change brought about by high pressure on the fluorescence of a dissolved dye, 9 amino acridine (9AA). The choice of this particular dye was justified by three important facts: first, the high quantum yield of the dye in water (Q.Y. = 0.98); second, the dye has a lifetime accessible to our apparatus ($\tau_F = 16$ nsec); third, the dye possesses a structured fluorescence (thus spectral peak shifts with pressure can be more easily monitored). Both the fluorescence spectra and lifetime of 9-amino acridine in water were studied at 298°K up to 30 kbar. In addition, fluorescence measurements were made at 1 atmosphere as a function of pH, temperature, and crystalline state.

At one atmosphere and room temperature 9-amino acridine at a neutral pH exhibited a spectrum consisting of 3 peaks centered at 440, 455 and 480 nm (see Fig.7). The 10^{-3} M solution showed a slight red shift and broadening until reaching 10 kbar. At this pressure the sample emission intensity dropped dramatically and the peak maximum shifted red from 455 to 510 nm. At pressures from 10 to 30 kbar spectral changes were not noticed. When the high pressure was released the spectrum returned to the same form as prior to the pressure cycle indicating a reversible change had occurred.

The lifetime of 9-amino acridine under the same conditions followed the same pattern: no change in $\tau_F = 16$ nsec below 10 kbar, and a drop to ≤ 4 nsec above 10 kbar. The lifetime shortening is also observed by lowering the temperature or examining the crystal. Similarly, the spectra under these conditions correspond to those induced by pressures above 10 kbar. The

spectra were also checked as a function of pH (3-13) and dilution, which produced only minor changes in intensity distribution or peak location. Crystals of 9-amino acridine were also studied at one atmosphere and under high pressure at 298°K. At 10 kbar and 298°K the spectrum of the crystalline dye sample looked very similar to that of the solution at 10 kbar at 298°K.

The change in the fluorescence of 9AA in water at 10 kbar and 298°K can be explained as being the outcome of a phase change that the solvent undergoes at that pressure and temperature. Bridgman noted that water will solidify at room temperature at 10 kbar in going from the liquid state to Ice VI. Therefore, the change in the fluorescence of 9-amino acridine is an optical observation of freezing which previously had only been measured by a volume change.

The related experiments suggest that the luminescence change upon freezing is not due to protonation but rather aggregation, as previously observed for perylene in cyclohexane solutions. The binding mode would probably be hydrogen bonding between the amino group of one molecule and the ring nitrogen on another, thereby breaking up the water structure around the solute molecules in the fluid state. It should be noted that this is not a gradual process but rather a sudden onset of dye aggregation at the phase transition point.

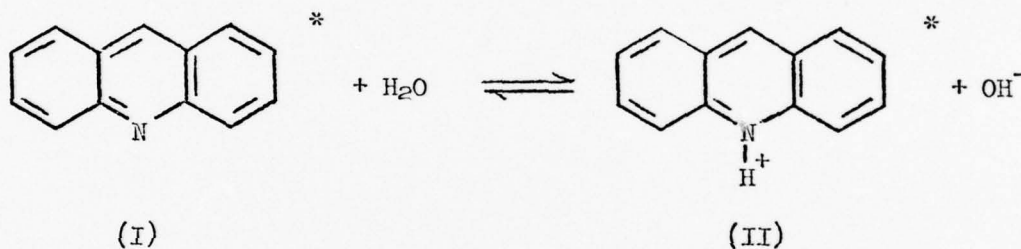
Aside from the inherent importance of the effect of a pressure-induced environmental change on the luminescence of a dye in water, these results also point toward the possible utilization of fluorescence as a sensitive monitor of freezing of other water solutions at different temperatures. Such an approach to phase transitions could be more informative about the initiation and completion of a phase change. In addition, the P-T mapping of such solutions might reveal new information about the solvent role and different ice polymorphs in physico-chemical processes.

B. Fluorescence of Acridine in Water at High Pressure

It has been shown that the basicity of certain aromatic molecules differs in the ground electronic state versus excited electronic states. Acridine, the nitrogen heterocyclic analog of anthracene, is an excellent example of a molecule whose emissive characteristics are controlled by the fact that it becomes more basic in the first excited state and that once in the excited

state a new proton transfer equilibrium (relative to the ground state equilibrium) is established in protolytic environments.

The pressure-unperturbed (1 atmosphere) luminescent properties of acridine have been studied by many investigators and the basic nature of the excited state proton transfer is understood. Fluorescent lifetime measurements of acridine have been made under conditions of varying temperature, pH, concentration and solvent. In addition, the fluorescence emission has been studied as a function of pressure by our laboratory in a polymer matrix (polymethylmethacrylate) and by Weller in an aqueous solution. Our objective was to study the effect of a pressure perturbation of the excited state equilibrium of acridine by means of both fluorescence emission (steady state) and lifetime (time dependent) measurements.



A shift in the excited state equilibrium between the two species should be observed with the application of high pressure and monitored by the different fluorescent properties of I and II. The fluorescence emission of 10^{-4} M solutions of pH = 3.1 (II), 7.0 (I and II), and 13.0 (I) were monitored as a function of pressure up to nearly 10 kbar and it was found that the emission of both the pH = 3.1 and 13.0 solutions were effectively unchanged with pressure. However, the spectrum of the pH = 7.0 solution shifted red considerably with the application of pressure (Figure 8). Using the relative intensities at two wavelengths, representing emission from the respective species, for the spectra of the pH = 7.0 solution at 1 atmosphere and 2.5 kbar, we are able to determine a ΔV of -25 cc/mole for the equilibrium given in the above equation.

In addition to spectral measurements the effect of pressure on the fluorescent lifetimes of acridine solutions was also determined. The single decay component at both extremes of the pH range both shorten as the pressure on the solution is increased. Species II is characterized by $\tau = 27.5$ nsec at 1 atm and $\tau = 22.5$ nsec

at 10 kbar; Species I by $\tau = 11.3$ nsec and 8.4 nsec, respectively.

However, at pH's between 3 and 13 it is possible to isolate two distinct decay curves using the appropriate Corning filters (7-54 for emission in the blue and 3-73 for the green emission). The blue decay curve corresponds primarily to the non-protonated species I and the green emission decay curve corresponds to the emission of the protonated species II. The singlet decay, of course, also reflects the kinetics involved in the basic equilibrium between the two species. As with the spectral shift with pressure for the pH = 7.0 solution, we also observed a change in the decay curves as the pressure is increased.

The kinetic analysis of the decay components was attempted in a manner described previously for pyrene in ethanol and cyclohexane to obtain the specific rate constants for the excited state proton transfer and for the de-excitation processes of both excited state species. Unfortunately, the data was such that the computer fit did not permit a unique assignment of the various parameters as a function of pressure. A qualitative view of the pressure effect on the time dependent measurements can be obtained from Table III, where the pseudo-lifetimes quoted correspond to the time necessary for the intensity to decrease from an initial value of I to I/e . The pseudo-lifetimes were measured as the pressure was increased and listed for a pH = 7.0 acridine solution in Table III.

TABLE III

Pressure	Pseudo-Lifetimes (nsec)	
	Species I	Species II
1 atm	11	22
2.5 kbar	8	26
5.0 kbar	6	29
10 kbar	7	22

The trend in the pseudo-lifetimes is such that with pressure the decay of the non-protonated species I shortens, whereas the protonated emission decay is observed to lengthen, at least up to 5 kbar.

Acridine in the ground state has a $pK = 5.5$ and becomes more basic in the excited state with a $pK = 10.3$. Pressure clearly favors the formation of the protonated species in the excited state, evident from the red shift in the emission to an extent that the high pressure emission best corresponds to the spectrum of the protonated species (at 1 atm and at low pH), and from a lengthening of the pseudo-lifetime (where the protonated species emits) that approaches the 1 atmosphere lifetime of the acridine solution at low pH. Thus, pressure is able to induce the excited state acridine molecule to acquire a proton more readily. The driving force in this enhancement of proton affinity seems to be that pressure, in agreement with Le Chatelier's Principle, favors the formation of more ions in solution since enhancement of charges is accompanied by a contraction, or electrostriction, of the surrounding solvent molecules. Water molecules are more densely packed around ions than around the corresponding uncharged species, and this contraction helps compensate for the compressive stress brought about by the increase in external pressure. The ΔV we obtained for the excited state transfer is similar in magnitude to those of ground state proton transfers measured by others.

These two projects represent our first pressure studies of fluorescence in water. The early termination of this contract did not permit a complete exploration of other fluorescent probes in different environments. We have monitored the fluorescence upon freezing of dilute water solutions (at one temperature only) to discern the impact of rigidity vs polarity on fluorescent properties and discovered the diminished solubility of the solute in the frozen state. Further experiments involving the simultaneous change in P and T are necessary to determine the effect of solvent polarity and relaxation on luminescence and to reach a clearer understanding of why these spectral parameters characterize the probe's environment in the fluid and frozen state. There appear important implications for hydrophobic interactions in micelles and enzymes as well as other catalytic systems in water. But the pressure work must be extended before the feasibility of practical and important applications of the pressure parameter as a modifier of catalytic processes can be demonstrated.

The several years of ONR support for this spectroscopic pressure research has led to significant advances in experimental techniques and to many interesting pressure effects on materials which can be generalized, at least

for the class of aromatic hydrocarbons. The preliminary pressure studies of aqueous solutions also promise interesting results on the molecular level and the distinct possibility of technological applications in the realm of kinetic processes in water.

Figure Captions

Figure 1 : Formula and Structure of Several Organic Molecules

Figure 2 : Cross-section of high-pressure optical cell.

Figure 3 : Ruby R_1 Line Shift at room temperature as a function of applied pressure.

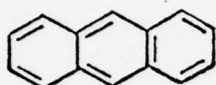
Figure 4 : Schematic diagram of liquid cell; 2.242 in diameter and 1.460 in length. The cell body and components are made from beryllium-copper, heat treated to RC 40.
(1) sapphire windows; (2) mushroom plug; (3) packing rings (copper, teflon, brass); (4) triangular support rings (beryllium copper); (5) threaded outer plug; (6) sample capsule holder (stainless steel); (7) Aminco super pressure tubing; (8) gland nut; (9) sleeve.

Figure 5: Liquid Sample Capsule. (1) sample capsule holder; (2) quartz sample capsule (contains sample solution); (3) teflon piston; (4) tightening screw; (5) mushroom plug; (6) packing rings.

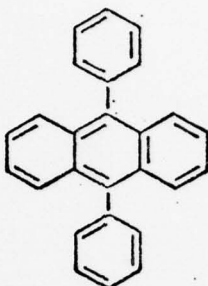
Figure 6 : Block diagram for transient luminescence measurements at high pressure. (A) High-voltage power supply for the nitrogen laser;⁵ (B) High-pressure optical cell;⁶ (C) TRW 38A relay lens assembly consisting of lenses(L), filters(F), silvered mirror(M), and iris diaphragm(S); (D) Amperex 56 AVP photomultiplier housed in a Ortec 269 base assembly with magnetic shield; (E) RCA-1P28 trigger photomultiplier; (g) variable delay; (H) fixed delay; (K) Tektronics 564B pulse sampling oscilloscope with 3S1 and 3T4 plug-in units; (Q) quartz plate.

Figure 7 : Spectra of a 10^{-3} M solution of 9 amino acridine in water at room temperature, and at one atmosphere (—) and at 10 kbar (----).

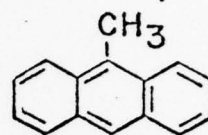
Figure 8: The fluorescence spectra of 10^{-4} M aqueous acridine solution at pH = 7.0 and 298° for pressures of 1 atm and 10 kbar. The intensities are normalized for both spectra.



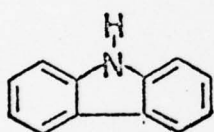
Anthracene
 $C_{14}H_{10}$



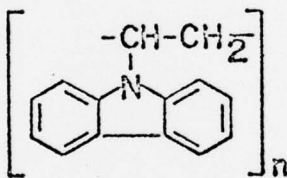
9,10-Diphenylanthracene
 $C_{26}H_{18}$



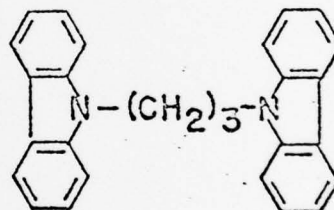
9-Methylanthracene
 $C_{15}H_{12}$



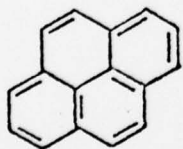
Carbazole
 $C_{12}H_9N$



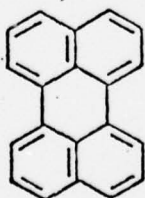
Poly(N-vinylcarbazole)
 $(C_{14}H_{11})_n$



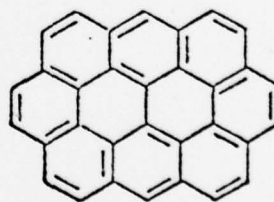
1,3-Bis(N-carbazolyl)
propane
 $C_{27}H_{23}N_2$



Pyrene
 $C_{16}H_{10}$



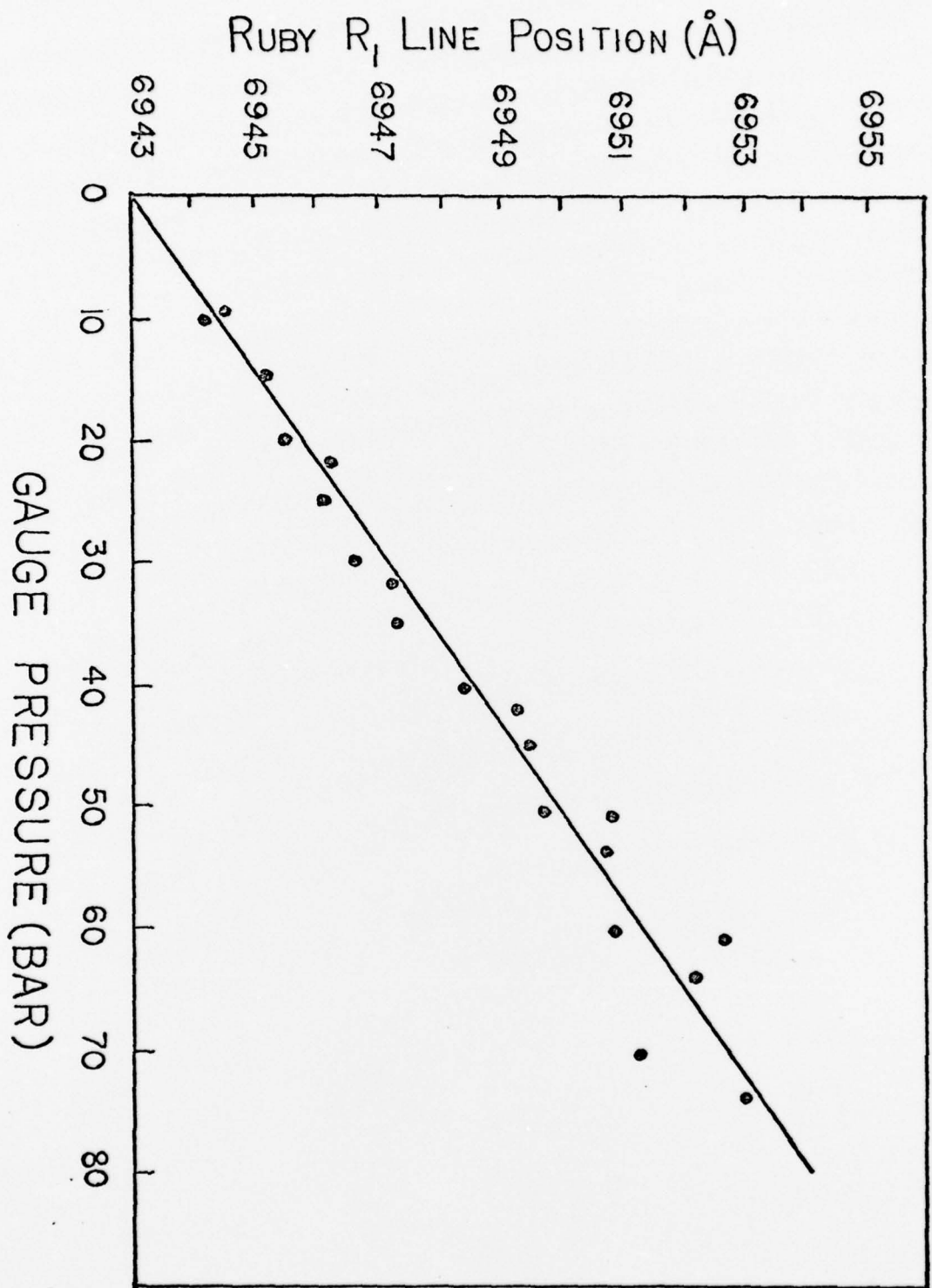
Perylene
 $C_{20}H_{12}$



Ovalene
 $C_{32}H_{14}$

Figure 2

- (A) Outer steel jacket, carpenter No.883 tool steel, heat-treated to Rockwell "C"-55.
- (b) Threaded piston guide, brass.
- (C) Stationary threaded piston sleeve, crucible La Belle silicon No.2 tool steel, heat-treated to Rockwell "C"-58.
- (D) Window retainer, made from $\frac{1}{2}$ " alloy steel shoulder screw to obtain hexagon socket. Ground and lapped to 2 microfinish on interface with window.
- (E) Teflon gasket.
- (F) Window vacuum tubes, stainless steel type 304.
- (G) Three-diameter window ports, filled with NaCl.
- (H) Tungsten carbide piston, Carboloy No.883 with .002" minimum interference fit in piston sleeves. Sleeves heated to 175°C to facilitate press-fit.
- (I) Moving piston sleeve. Crucible La Belle Silicon No.2 tool steel heat-treated to Rockwell "C"-58.
- (J) Disc, ground from high-speed steel drill blanks.
- (K) Insert, vacuum-melted crucible La Belle silicon A151 S-5 tool steel heat-treated to Rockwell "C"-60. Shrink fit in outer jacket "A" with .0045" interference. Jacket heated to 150°C, insert cooled in liquid nitrogen to facilitate assembly.
- (L) $\frac{1}{4}$ " diameter x $\frac{1}{4}$ " long cylindrical polished sapphire, Linde-oriented.



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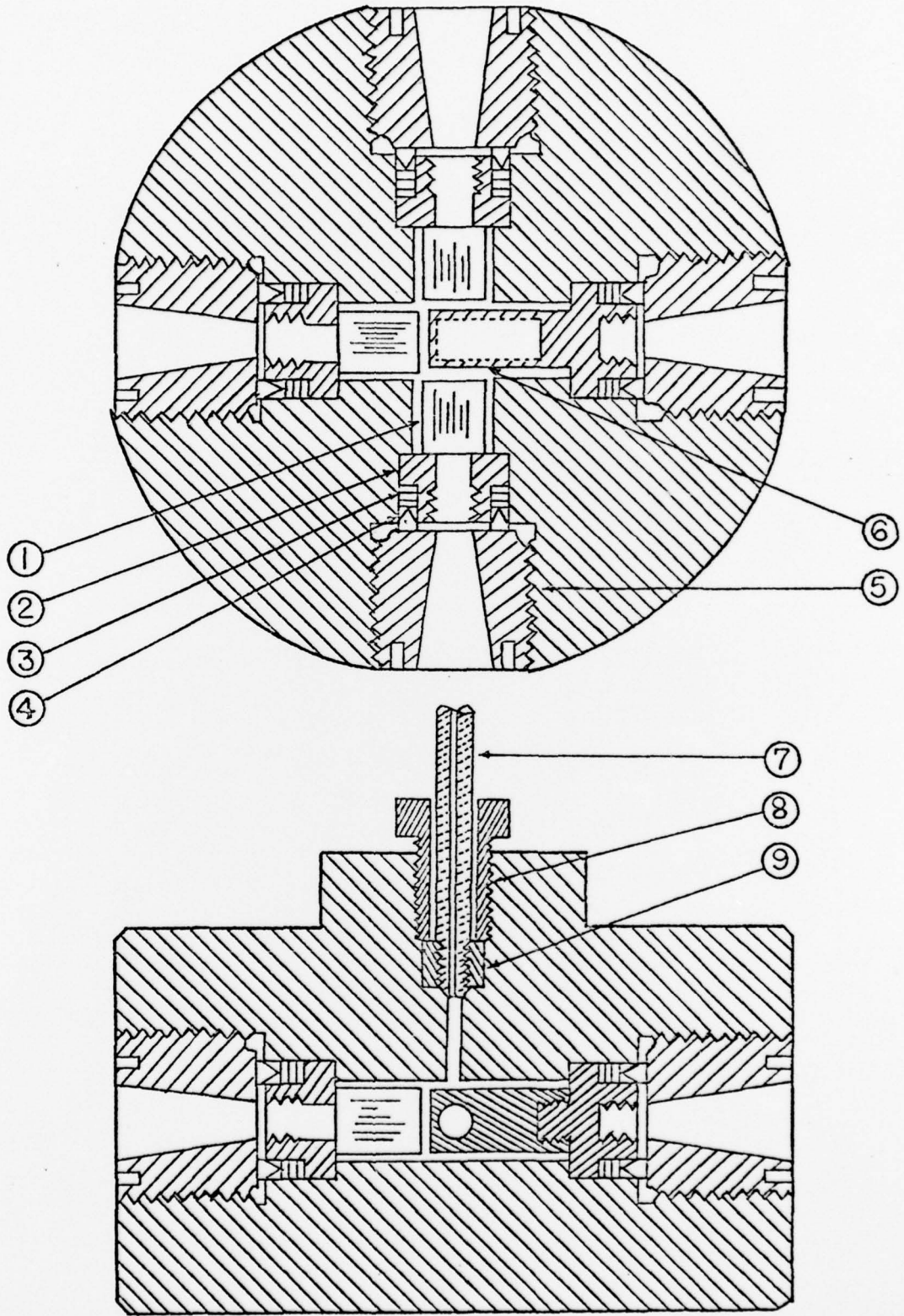
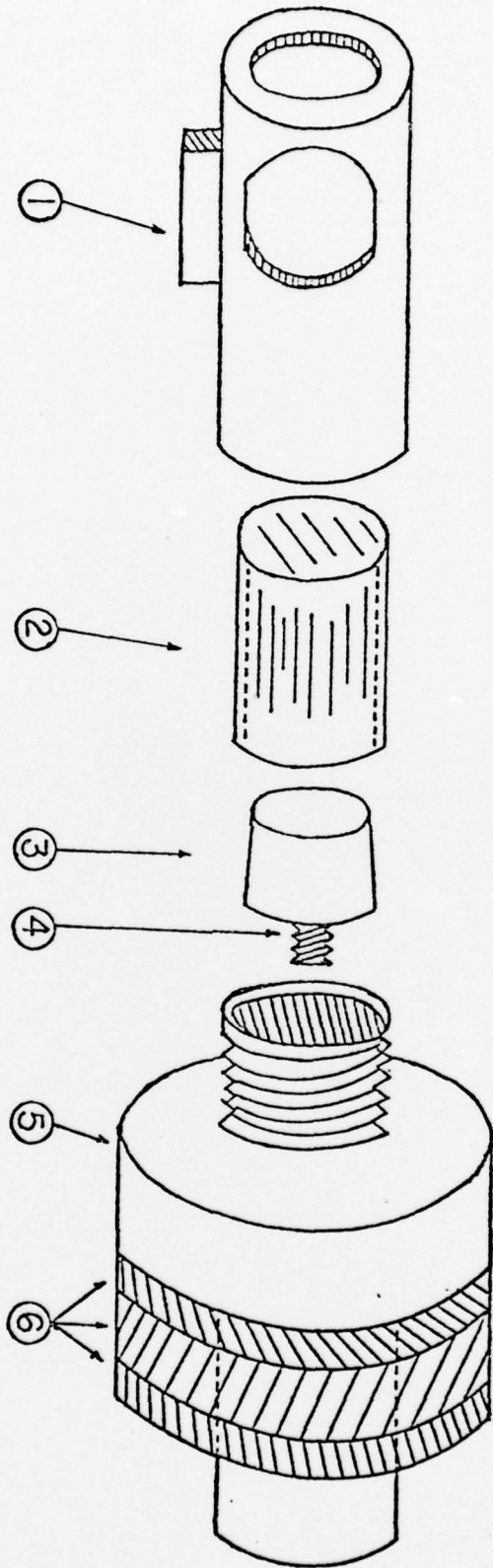


Fig. 4



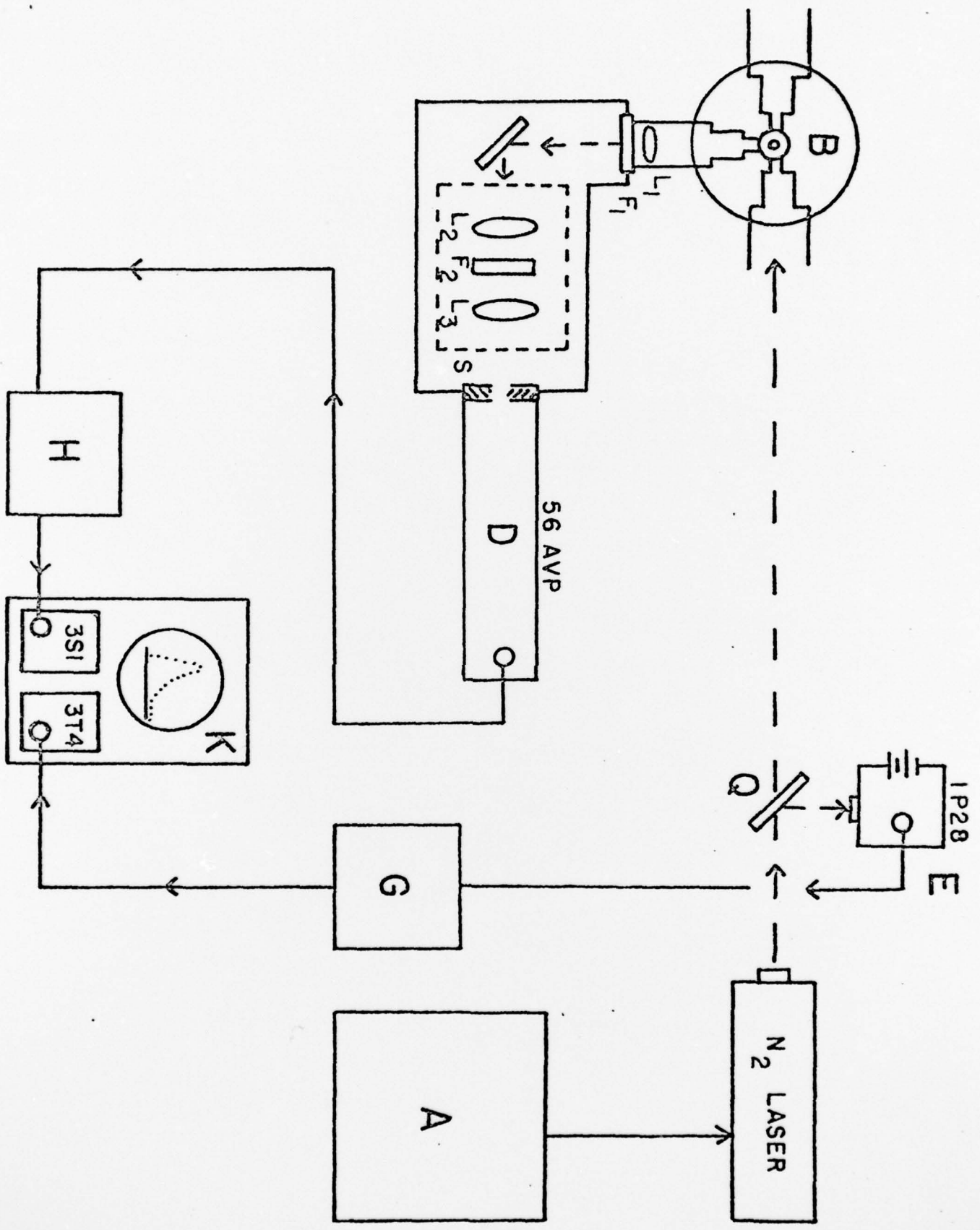


Fig 6

Fig. 7

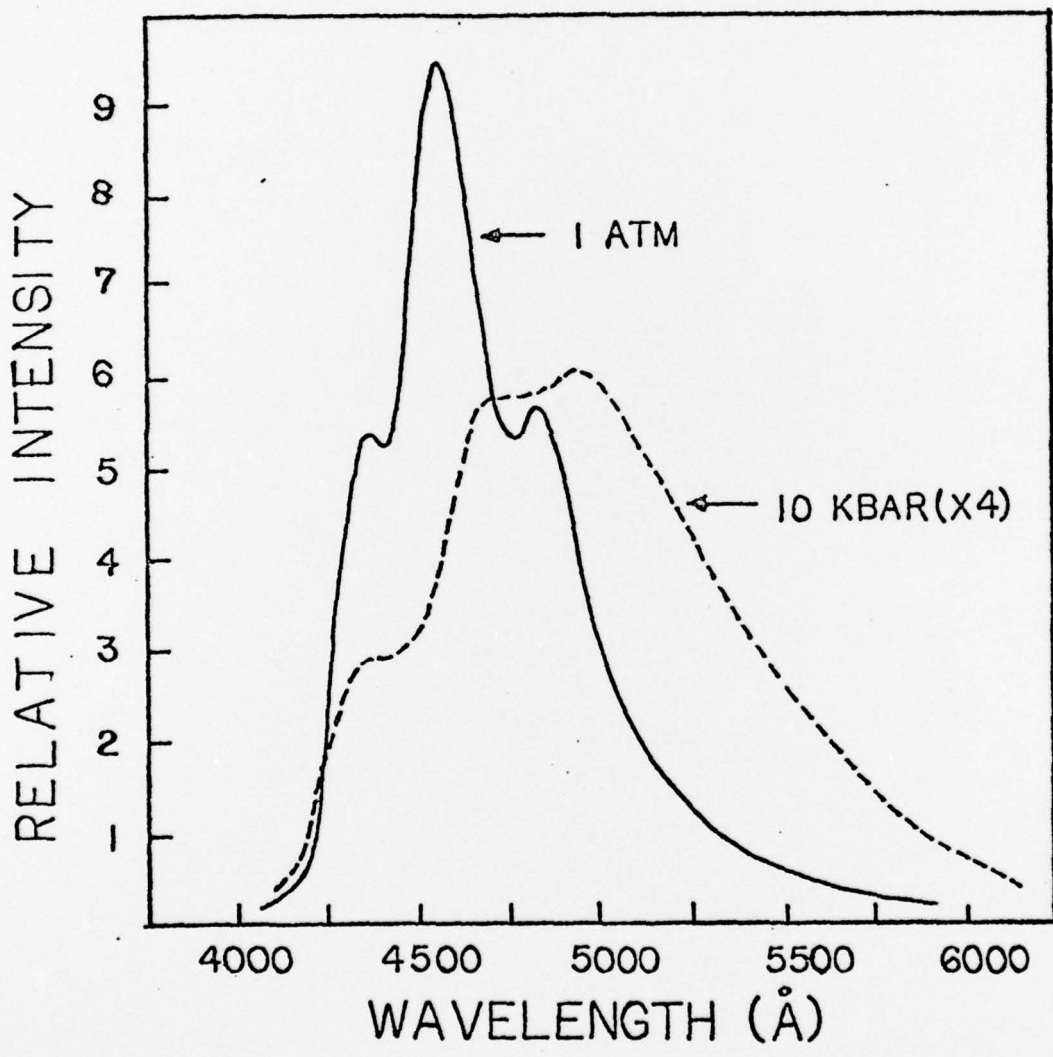
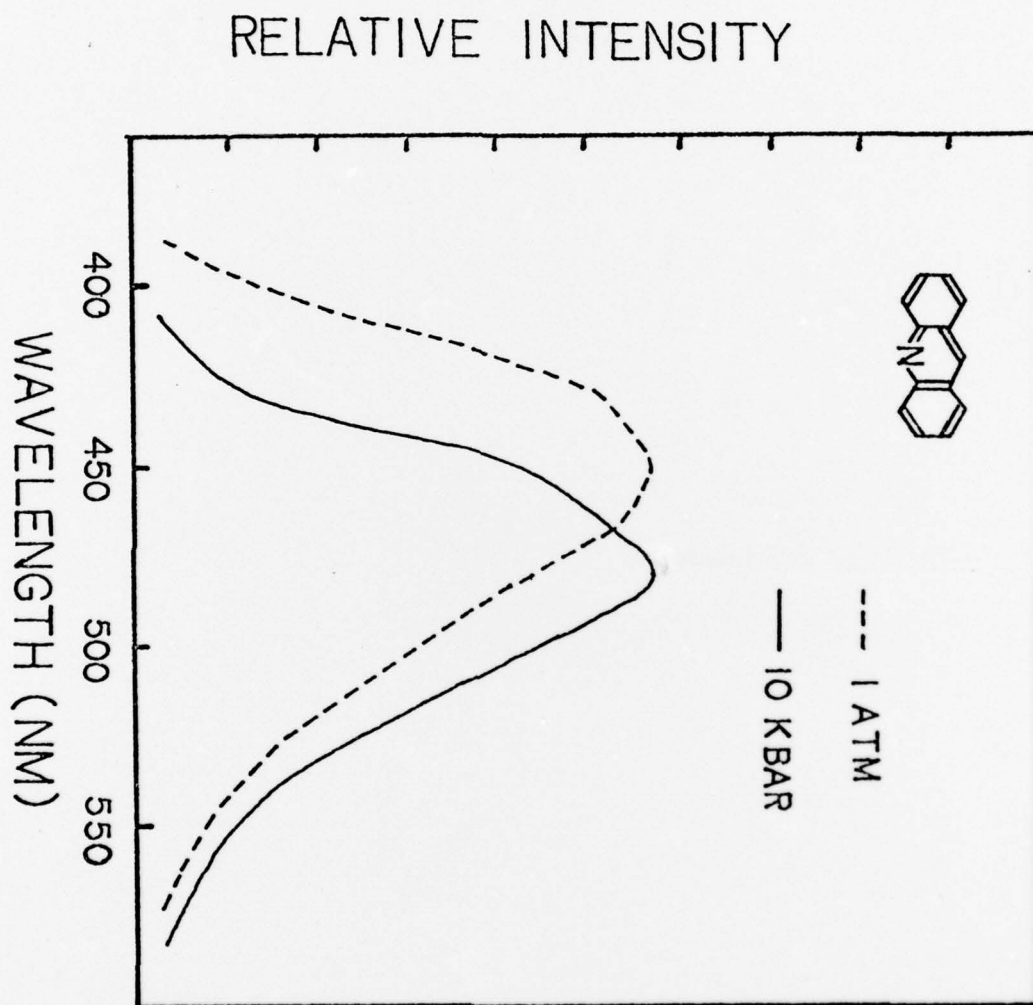


Fig 8



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