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LIGHT SCATTERING BY LIQUIDS AND MOLECULAR SOLIDS

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Light Scattering by Liquids and Molecular Solids

A Dissertation submitted in partial satisfaction
of the requirements for the degree of
Doctor of Philosophy
in
Physics
by
Stanley Leland Shapiro

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ABSTRACT

Light Scattering from Liquids and Molecular Solids

by

Stanley Leland Shapiro

Measurements of the frequency broadening caused by molecular rotations have been made in liquid carbon disulfide and in liquid mixtures of carbon disulfide and carbon tetrachloride by observing scattered light from an Ar^{+} laser at 4880Å. The spectral shape of the scattered light has been found to be nearly Lorentzian. Half-widths of the scattered radiation in carbon disulfide range from about 0.1 /cm^{-1} near the triple-point to 6/cm^{-1} near the boiling point. Addition of carbon tetrachloride to carbon disulfide at room temperature causes the half-widths to decrease. Measurements of the frequency broadening have been used to calculate relaxation times for the attenuation of molecular rotations in liquids. These measurements show that the relaxation time is proportional to the viscosity of the liquid and inversely proportional to the temperature of the medium, a result in agreement with a theoretical prediction of Debye.

Measurements of the relative intensities of the Rayleigh line, the Brillouin lines, and the depolarized orientation scattering line have been made in liquid carbon disulfide. These studies have been used to obtain information about the angular correlations between

molecules in liquids. Such measurements in liquid carbon disulfide indicate that the molecules tend to align with their internuclear axes perpendicular to each other.

Vibrational Raman scattering ~~has~~ been excited in liquid and solid carbon monoxide and nitrogen, and orientation scattering has been studied in liquid oxygen. The vibrational Raman line in solid nitrogen occurs at 2327.5 ± 0.5 cm^{-1}, the same position as the liquid. The Raman line in both liquid and solid carbon monoxide occurs at 2138 ± 0.5 cm^{-1}. These vibrational frequencies are about 4 cm^{-1} less than the gaseous phase frequencies, the shifts undoubtedly arising from the attractive Van der Waals forces. Orientation scattering results indicate that the molecules in liquid oxygen rotate quite freely.

Brillouin scattering measurements ~~have~~ been made in room temperature liquids in which an Ar^+ laser has been used as a source of excitation. A He^3-Ne laser has been used to excite Brillouin scattering in liquid NH_3 and ND_3. Measurements of the Brillouin shifts have been used to calculate the velocity of sound of the phonons in the gigacycle frequency range. Velocity dispersions at about 2Gc in liquid NH_3 and ND_3 have been postulated to be due to a structural relaxation of the liquids.

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I. INTRODUCTION

Einstein[1] considered the problem of light scattering in gases and liquids in 1910 and obtained formulas relating the intensity of the light scattered to density fluctuations in the medium. Debye[2] developed a model of lattice vibrations in solids in 1912, and in 1922 Brillouin[3] gave a comprehensive treatment on scattering of light by solids in which he applied the general theory of scattering given by Einstein to show that the fluctuating density waves of Debye would give rise to a quite interesting scattering phenomenon. He predicted that monochromatic light passing through solids and liquids may be shifted slightly by discrete frequency changes due to scattering by acoustic waves in the media. The frequency shift corresponds to the frequency of the acoustic waves in the media. Mandelstam[4] independently predicted these components in 1926. Scattering from acoustic waves is called Brillouin scattering in the United States and Western Europe and Mandelstam-Brillouin scattering in the Soviet Union.

In 1930 Gross[5] was able to experimentally verify the predictions of Brillouin and Mandelstam. Gross resolved the Rayleigh line into a triplet composed of a central component, often referred to as the Rayleigh line, and two side components, the Brillouin lines. Landau and Placzek[6] recognized that the central component is caused by entropy fluctuations which propagate with zero velocity so that there is no frequency shift. They showed on the basis of thermodynamic arguments that the ratio of the intensity of the central component, I_C, to that of the two Brillouin components, $2I_B$, should be given by $I_C/2I_B = C_p/C_v - 1$, where C_p and C_v are the specific heats. Modifications of the Landau-Placzek relation to account for dispersion of sound waves have been put forth by Fabelinskii[7] and by Cummins and Gammon.[8]

Raman[9] discovered in 1928 that when an intense beam of monochromatic light is passed through a material the light viewed at right angles has additional components symmetrically placed on both sides of the original wavelength, the lines being characteristic of the medium through which the light has passed. The energy shifts are characteristic of the molecular levels of the system so that the Raman effect has become a powerful tool for investigating the structure of matter. Krishnan and Raman[10] noticed that in some liquids the vibrational Raman lines of the molecules have a broad diffuse wing. In gases instead of a diffuse wing about the vibrational line there were sharp distinguishable lines attributable to molecular rotations. Thus Krishnan and Raman concluded that the diffuse wing in liquids arose from molecular rotation. In 1941 Leontovich[11] developed a theory of light scattering by anisotropic molecules in liquids. Rytov[12] extended Leontovich's theory by using correlation theory to describe the wings of the Rayleigh line. According to Rytov's formulation, shear deformations result in fluctuations of anisotropy which scatter light. Ginzburg[13] has pointed out, however, that a medium consisting of anisotropic molecules can scatter light as a result of fluctuations in the orientations of the axes of the molecules.

Fabelinskii[14] carefully analyzed the Rayleigh wing in many liquids and was able to show that the wing was Lorentzian in shape and that relaxation times calculated from the frequency distribution of the scattered light were approximately given by the Debye relaxation time. Starunov[15] in 1964 carefully analyzed the spectral distribution of the Rayleigh wing and showed that there was an increase in the intensity of the scattering at frequency shifts from 50 to 100 cm^{-1} in some liquids. Since the position where the intensity increased agreed with positions of the lattice vibrations in the crystalline phase of the liquids, Starunov attributed the intensity increase to local structure in the liquid or "quasi-crystalline" lattic vibrations. Porto[16] has also observed these molecular bands in liquids.

During the last few years there has been an increased interest among physicists and chemists in the study of light scattering from liquids and solids. This increased interest can be traced for the most part to the advent of the laser. The laser is on excellent light source for scattering experiments since it is intense, monochromatic, and has small beam divergence. Because of these exceptional properties, measurements which were previously difficult are readily made, and measurements of higher accuracy are possible. First a discussion of some measurements made with gas lasers.

Kogelnik and Porto[17] obtained Raman scattering using a He-Ne laser as a Raman source in 1963. Spectra were obtained photograpically, the liquid samples of CS_2, C_6H_6, and CCl_4 being placed in the laser cavity itself because of the higher power inside the cavity. Leite and Porto[18] were able to photoelectrically record the Raman effect in liquids with the sample inside or outside the cavity. Only recently laser sources have become better for exciting Raman spectra than mercury sources. The newly developed rare gas ion lasers are intense enough to surpass mercury sources for exciting Raman spectra and are much more convenient to use.

Benedek et al.,[19] Chiao and Stoicheff,[20] and Mash et al.[21] used a He-Ne laser to excite Brillouin scattering in liquids in 1964. It was immediately apparent from these measurements that laser sources were superior to other available scattering sources. The velocity of sound in liquids was measured far more accurately than ever before. In addition velocity dispersions were measured as a function of the frequency of the phonons by observing the scattered light as a function of angle, and Brillouin line widths were measured for the first time. Line width measurements yield information on phonon damping processes, and relaxation times, which may be calculated from the velocity dispersion of the sound waves, yield information on the transfer of energy to vibrational and rotational modes of molecules or of changes in structure in the fluid. In addition Chiao and Fleury[22] measured the Brillouin shift as a function of the scattering angle and as a function of temperature and measured relaxation times for the transfer of acoustic energy to molecular modes and structural modes in liquids.

Striking success has been obtained recently in the study of Rayleigh light scattered by materials. The study of Rayleigh light scattering has been difficult because Rayleigh linewidths are typically only about 100 Mc in liquids at large scattering angles and become very small at small scattering angles. Using optical heterodyne techniques Cummins et al.[23] observed diffusion broadening of Rayleigh scattered light from large molecules suspended in a fluid. An equivalent optical resolution of 10^{14} was obtained allowing measurements of the linewidth at small scattering angles. This diffusion broadened Rayleigh linewidth was found to be proportional to $\sin^2(\theta/2)$, in accord with theoretical predictions. Later Lastovka and Benedek[24] used an optical heterodyne spectrometer to measure the Rayleigh linewidth in toluene as a function of angle and were able to show that the magnitude and angular dependence of the linewidth were in excellent agreement with an equation given by Leontovitch.[25]

Another problem receiving much attention is the light scattering by concentration fluctuations in binary mixtures (critical opalescence). In 1965 Alpert[26] reported that the linewidth of the scattered light from binary mixtures depended on the angle of scattering and the distance in temperature from the critical point. Debye[27] explained the spectral width dependence of the critical opalescence in binary mixtures in terms of diffusion ideas and showed that the width goes as $T - T_c$ where T_c is the critical point temperature and that the angular dependence of the linewidth is proportional to $\sin^2(\theta/2)$ where θ is the angle of scattering. In addition Ford and Benedek[27] looked at light scattering from pure SF_6 near its critical point and detected scattering due to entropy fluctuations which decay slowly near the critical region and were able to measure a correlation rate for the entropy fluctuations.

Accurate measurements of the depolarization of the Rayleigh line and Brillouin lines and of their intensity ratios may be obtained using a laser source.[29-33] Measurements of the ratios of the intensities of the Rayleigh to the Brillouin components were often found to disagree with the Landau-Placzek predictions, even for such simple liquids as CS_2 and CCl_4. Better results have been obtained when the Landau-Placzek relation is modified to take care of the effects of dispersion and electrostriction.[8] Dust must be carefully removed from liquids in order to obtain reliable results. Gornal et al.[34] have found that the disagreement with the Landau-Placzek relation in CCl_4 is due to a new nonpropagating mode which arises from the exchange of energy between the internal vibrational modes and translational modes and decays with a lifetime of the order of the relaxation time τ for the energy transfer. It gives rise to a broad line of frequency width $1/\tau$. When the intensity of this mode is added to the intensity of the Brillouin components, the Landau-Placzek relation is in good agreement with experiment in CCl_4. Starunov et al.[35] have explained the deviation in nitrobenzene as due to the depolarized orientation scattering which is very narrow in nitrobenzene.

Many new Raman processes in solids have been studied for the first time using lasers as sources of excitation. Henry and Hopfield[36] first reported Raman scattering from polaritons in GaP. The polariton is a mixture of a phonon and a photon whose wave vectors can no longer be described as a photon or phonon and occur in ionic crystals where transverse optical phonons and photons with nearly the same wave vector and energy are strongly coupled. Fleury et al.[37] have shown that magnons exhibit a Raman effect by detecting the light scattered by spin waves in the first and second order in FeF_2. Worlock and Porto[38] reported Raman scattering from F centers which provided direct information on the vibrational interaction of F centers.

In addition stimulated scattering processes have been studied using pulsed high power lasers. Second harmonic generation was achieved by Franken et al.[39] and third harmonic generation by Terhune et al.[40] Woodbury and Ng[41] discovered stimulated Raman scattering in nitrobenzene, the effect being explained by Eckhardt et al.[42] Stimulated Brillouin scattering from liquids was detected by Garmire and Townes[43] and by Brewer[44] and from solids by Chiao et al.[45] Stimulated Rayleigh scattering was described by Mash et al.[46] and by Bloembergen and Lallemand.[47]

The orientation scattering in liquids has been studied by Shapiro et al.[48] and Starunov et al.[35] using gas lasers. Because studies of the orientation scattering yield information on the motion of molecules in liquids, and measurements of the intensity distribution and depolarization of the scattered light give information relating to the structure of the liquid, orientation scattering was studied as a function of temperature in pure liquids. Shapiro and Broida[49] report measurements for CS_2 of the spectral distribution, depolarization, and ratios of the intensity of the Rayleigh and Brillouin components to the orientation scattering in Appendix I. Measurements in liquid mixtures of CS_2 and CCl_4 are also reported. Pecora and Steele[50] have related the depolarization of the scattered light to the angular correlation between molecules in liquids. Measurements of Shapiro and Broida in CS_2 show that angular correlations exist between CS_2 molecules and that perpendicular orientations of the internuclear axes are favored over parallel orientations. The orientation scattering has also been studied in liquid oxygen.

Raman scattering in low temperature liquids and solids has been studied quite extensively by J. C. McLennan and others.[51] Information on the fundamental molecular vibrational and rotational frequencies in liquids and solids has been obtained from such studies. Using a laser such studies are easier because the samples may be much smaller, the geometry is simplified, and the scattered light problem is reduced. Results on the Raman scattering from liquid and solid nitrogen and liquid and solid carbon monoxide are reported in section 3.4. The frequencies for vibration in solid carbon monoxide and solid nitrogen are reported for the first time using Raman techniques.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

2.1 The Ar^+ Laser and Power Supply

Recently it has been demonstrated that lasers are excellent sources for exciting Brillouin and Raman spectra for the following reasons: they are intense sources of monochromatic radiation; narrow exciting lines may be obtained so that very small line shifts may be measured as well as line shapes; the beam divergence of a laser is very small and experimental arrangements are considerably simplified as compared to a low pressure mercury source for exciting Brillouin or Raman spectra; and small samples may be illuminated with little difficulty with the laser. The rare gas lasers (argon, krypton, and xenon) have been shown to lase at extremely high output powers.

The Ar^+ laser which is the best known of the ion lasers was chosen as the exciting source in these experiments because high intensities may be obtained at two convenient exciting wavelengths - 4880A and 5145A. Photomultiplier tubes and film emulsions are very sensitive at these frequencies and in addition the intensity of the scattered light goes as the frequency to the fourth power of the incident radiation for all electromagnetic processes involving induced dipole moments.

A word of caution is in order on the use of the Ar^+ laser for exciting Brillouin spectra. One may obtain a sharp line from an Ar^+ laser either by building the cavity so short that very few modes will oscillate, for the rest will be outside the gain curve of the laser, or one can run the laser just above threshold where only a few modes oscillate. One can run the laser at medium powers and be content with a broad asymmetrical exciting line, or one can use beat techniques to observe the spectra. At very high discharge currents the exciting line of the Ar^+ laser becomes broad because many modes oscillate, and interferometric techniques cannot be used to resolve Brillouin spectra with such an exciting line. Thus for interferometric detection of Brillouin splittings a He-Ne laser or a Neodymium continuous laser may be more suitable for Brillouin measurements. However, techniques are being developed for choosing single modes in high power lasers, and it seems likely that an Ar^+ laser can be made adaptable to Brillouin measurements. In addition heterodyne techniques have been used to observe Brillouin components in liquid helium with an Ar^+ laser.[52]

Figure 1 shows the schematic for the Ar^+ laser used in this experiment. The laser is constructed entirely of quartz because of the intense heats generated by the high current of the argon discharge (metal tubes of the appropriate design also have been used).[53] The laser tube itself is 30 cm long and has a precision bore diameter of 2.5 mm (Wilmad Glass Co. of New Jersey).

The anode is constructed of tantalum and may be constructed of stainless steel, tungsten, or copper.[54] Since the only criterion for the anode is that it can take the intense heat generated by the discharge, the latter three materials are preferable to tantalum[54] for unnecessary problems are introduced by tantalum because it gives off hydrogen. As shown in Figure 1, the anode is a disc with a hole punched in it for the beam to pass through. At high currents the discharge also passed through the anode along with the beam so that the end of the quartz tube had to be cooled with water and air. This problem can be avoided by using a cylinder for the anode so that it traps the rapidly accelerating discharge.[54]

The cathode (RCA FF 6001B) is a nickel ribbon which has been coated with a mixture of barium and strontium carbonates suspended in an organic binder. The reason for the choice of the cathode is that this particular mixture of barium and strontium carbonates results in a high electron emission. Oxides of barium and strontium greatly enhance the electron emission from the cathode.[55] A power supply (Kepco #PR15-30M) capable of providing 15 volts and 30 amps was used to heat the cathode. In order to process the cathode the following technique was used: The tube was first evacuated, as exposure of the cathode to air after heating apparently ruins the cathode. By raising the voltage and the current the temperature of the cathode was then slowly increased. The pressure inside the tube first rises rapidly as the organic binder comes off. After the binder is driven off, the cathode is heated to a very high temperature (about 1300°C) for a few moments to reduce the carbonates to oxides and drive off some of the binder. Currents between 25 and 30 amps were used for this process. If the pressure starts dropping when the current is increased, then the current should be turned down immediately for the metals on the

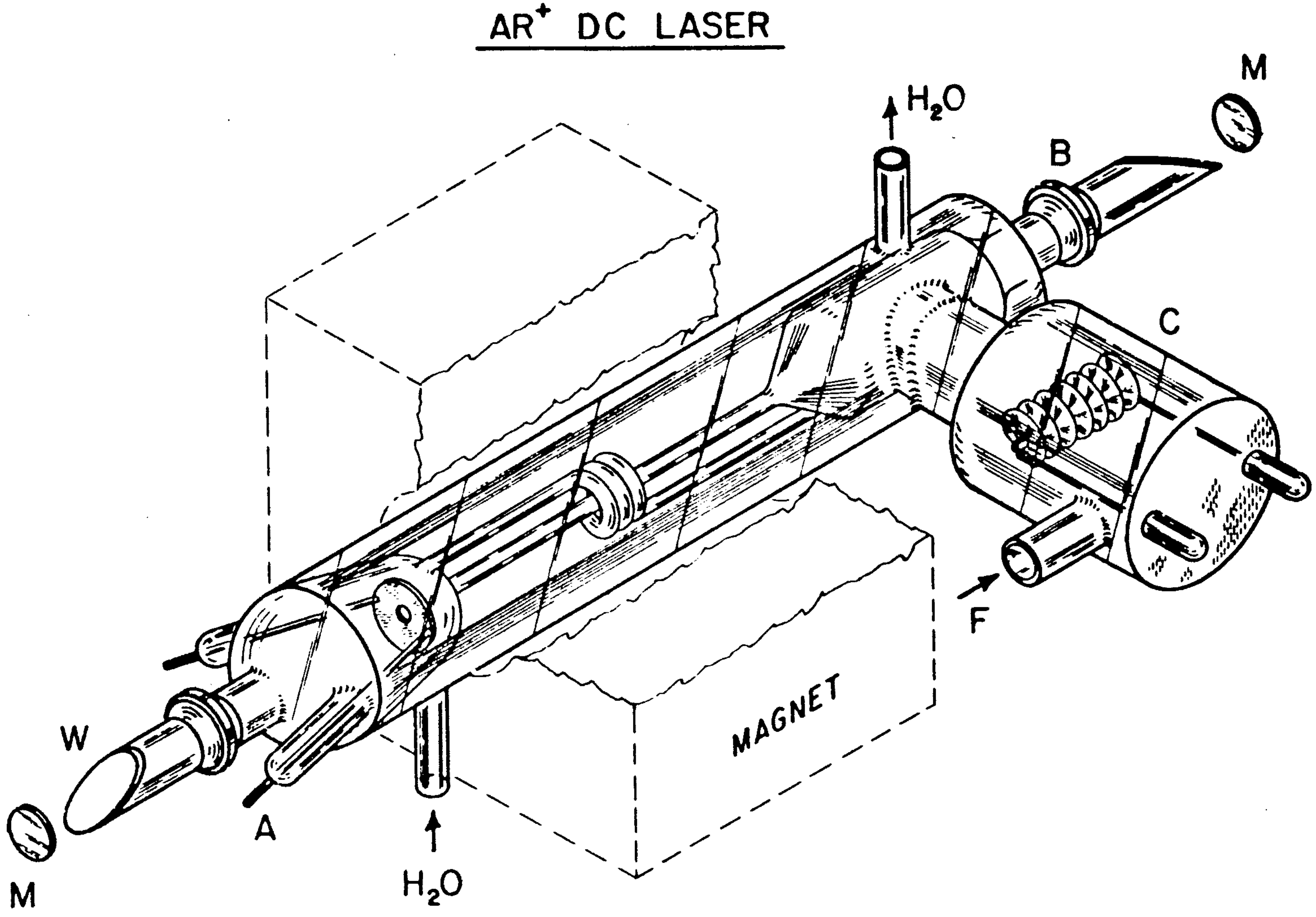


Fig. 1. Ar$^+$ DC Laser: A, anode; B, waxed ball joint; C, cathode; F, to fill system; M, mirrors; W, Brester windows.

cathode are gettering. The cathode is then run at 6 volts and 21.5 amps. At this current and voltage value, the temperature of the cathode was about 1100 to 1200°C, and the cathode has a long life Higher temperatures cause too rapid evaporation of the surface while too low a temperature results in localized surface emission at which the temperature is raised to excessive values.

An Ar^+ laser operates in a pressure range at which the mean free path of the ions is comparable to the radius of the discharge tube. There are two problems associated with running high currents in a quartz discharge tube. One is thermal as the amount of power to be dissipated at high current densities is very large. Another is that the quartz tube decomposes as time passes due to continual bombardment of the walls of the tube by the ions. The particular tube used in this experiment was refilled with argon every few weeks and often sooner because decomposition products can poison the cathode and because hydrogen was emitted by the tantalum anode. One method of avoiding decomposition of the quartz or at least prolonging the life of the laser tube is to run a magnetic field of 1000 to 2000 gauss coaxial with the tube.[53] Axial magnetic fields prevent diffusion of ions to the walls of the tube by constraining the discharge. Furthermore axial magnetic fields increase the charge particle density resulting in a greater pumping rate. Larger population inversion results so the laser output increases. However, at very high magnetic fields, collisional de-excitation by electrons dominates so that the laser output goes down. It is clear that at a certain magnetic field no diffusion of the ions to the wall will take place so no gain in prolonging the life of the tube would ensue by increasing the magnetic field. There is a compromise field that one should use and it is about 1000 to 2000 gauss.[53] The laser used for these experiments had a magnetic field of 1020 gauss running coaxial to the laser tube. The magnet (Ogallala Magnet Co.) was 30 cm long so it covered the length of the discharge tube. For our tube the magnetic field enhancement was measured to be four or five for the same current. The voltage needed for a given discharge current drops when the magnetic field is on. It would appear from the figures of Labuda et al.[53] that a magnetic field of about 1500 gauss would be slightly better (about 30% increase in output) than a 1000 gauss field for this particular tube. The magnetic field enhancement factor becomes more important for large bores--for a 1mm bore the enhancement factor is about 1.5 for an axial field of 2000 gauss while for a 5mm bore the enhancement factor is greater than one order of magnitude.

The pressure at which maximum output is obtained is a complicated function of the bore of the tube and of the discharge current. At a given discharge current, there is an optimum pressure for maximum light output, but this pressure changes for different discharge currents. Thus one must optimize the pressure corresponding to the particular discharge current in the tube. The pressures used in this laser ranged from 200 microns to 1 mm of argon gas. A typical pressure used was 400 microns when the discharge current was 5 amps. At higher currents the optimum pressure increases. The pressure was measured by a Pirani vacuum gauge (GP-140, Consolidated Vacuum Corporation) which was calibrated using argon gas. If one uses great care with such gauges, avoids contaminating them, and leaves them on only when taking a measurement, their calibration may be maintained to sufficient accuracy over long periods of time. Brewster windows were inserted in the laser cavity to cut down losses due to reflection. Because Brewster windows discriminate according to the direction of the electric field vector, the light emitted was partially polarized. For currents just above threshold level the gains exceeded the losses for only the component with electric field vector perpendicular to the plane of scattering and hence the light was polarized 100% perpendicular to the plane of scattering. For high currents, however, the beam becomes depolarized because the gains become so high that even the lossy reflected polarization component lases. In fact the laser lased with an output mirror of 70% reflectivity with a threshold of about 5 amps. If a polarized beam is desired for polarization measurements, a polarizer is inserted and polarized appropriately.

The laser contained a return coil which is the helical shaped coil in Fig. 1. The purpose of the return coil is to eliminate cataphoresis - differential pressure build up due to ions and electrons migrating to opposite electrodes. It was found with a short laser tube without a return coil, that when the discharge was turned on, it would lase at first, but the output would decrease and finally be eliminated altogether as cataphoresis sets in. The return coil should be large for maximum efficiency in cutting down cataphoresis. In the model shown in Fig. 1 the coil was only 4 mm I.D. A later model had a coil which was 15 mm I.D.

In order to dissipate the heat generated by the discharge, the tube was surrounded by a water jacket. For more efficient cooling the laser tube should be surrounded with a tube which is just larger than it so that water will flow very quickly over it. This rapid flow design was incorporated into a later laser design.

The laser fill system was simple, consisting of a bulb of argon near atmospheric pressure which was closed off with two stopcocks having a small volume located between them and was designed to give appropriate pressures when the volume was released to the total volume of the system. In practice one stopcock was opened filling up the region between the two stopcocks. The top stopcock could then be turned slowly and any pressure desired could be obtained by allowing the pressure in the system to go up to the value as measured by a Pirani gauge. A vacuum system consisting of an oil diffusion pump, a forepump, and a dewar trap was used to pump down the laser before filling it with argon. This system was capable of pumping down to pressures of better then 1×10^{-6} torr when the trap in the system was empty and pressures lower then 1×10^{-7} torr when the trap was filled with liquid nitrogen or oxygen.

Plane mirrors of 91%, 94%, and 98% reflectivity at 4880Å were used at the output end of the cavity while a mirror of 99.7% reflectivity at 4880Å and a radius of curvature of 1.47 m was used at the other end of the cavity. All the mirrors were purchased from the Spectra-Physics Co. and descriptions of different mirror configurations and how to choose mirrors for different bores and cavity lengths are contained in Spectra-Physics Bulletin No. 2.[56] Although the discharge lased continuously in six or seven lines, the only line used for exciting spectra was the 4880Å line of the Ar^+ ion as over 50% of the output power was contained in this line at the currents used to run the laser. At very high currents, the 5145Å line becomes very intense, however.[53]

The intensity of the beam was monitored with an RCA 929 phototube. A filter was used to isolate the 4880Å line and other filters were used to attenuate the beam. Two ninety volt batteries were connected in series to provide the phototube voltage, and the signal from the phototube was fed into an amplifier. The output power of the beam could be held stable to ±1%.

A high voltage, high current power supply was built to operate the laser. The schematic for the power supply is shown in Fig. 2. The power supply was capable of delivering 12 amps at 500 volts. By adjusting a variable resistor between zero and sixty ohms, currents in the range from 1 to 12 amps could be obtained. The limitation to the current is set by the rectifiers which can take a forward current

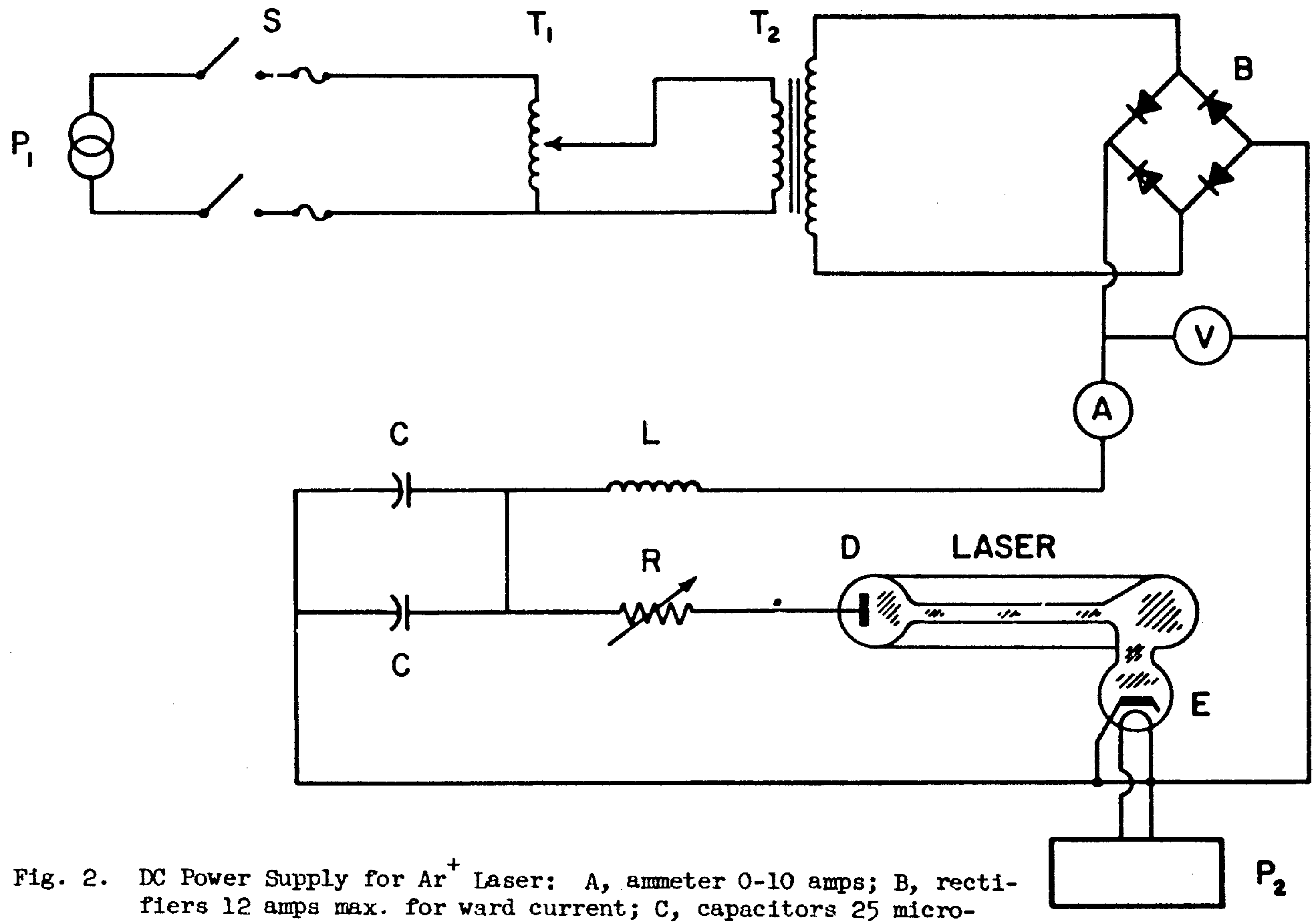


Fig. 2. DC Power Supply for Ar^+ Laser: A, ammeter 0-10 amps; B, rectifiers 12 amps max. for ward current; C, capacitors 25 microfarads; D, tantalum anode; E, cathode; L, inductance 64 mh at 5 amps; P_1, 208V, 50 amps; P_2, power supply 0-15 volts, 0-30 amps; R, variable resistor 0-60 ohms; S, double pole switch; T_1, transformer 0-280 volts, 20 amps max.; T_2, transformer 240 volts to 504 volts; V, voltmeter 0-500 volts.

of 12 amps. Although the power supply is filtered, more output power from the laser results if a stable discharge is obtained without a filter. This is because the output of the laser goes up rapidly as the current in the discharge increases. The output from the power supply had a very flat DC level, and thus the discharge was very stable, even at currents of less than 1 amp.

Another approach to building ion lasers has been reported by Goldsborough et al.[57] who use RF excitation for their discharge. RF excitation helps alleviate several problems. Since there is no anode or cathode, sputtering of the anode or problems associated with electron emission of the cathode are eliminated. In particular large cathode chunks may fly off at high currents and contaminate the tube.[58] In addition quartz tubes last longer when excited with RF rather than DC excitation. When quartz tubes break in DC tubes, they usually break where the discharge tube flairs out near the cathode end. Decomposition is especially obvious to the eye at this location.

There have been other approaches for increasing the output of Ar^+ lasers. Thus Bell[59] has shown that if one uses a magnetic field and antireflection coated windows which are oriented perpendicular to the laser beam, the laser output can be increased by a factor of 1.5. This is because the magnetic field splits the lines (Zeeman effect) and such a window arrangement does not exhibit loss to Zeeman split lines. One can go one step further by eliminating windows and using mirrors inside the laser tube. This can be done using a bellows arrangement. If the tube is clean, the troublesome problem of the reflectivity of the mirrors changing due to contaminants in the air can be eliminated.

2.2 Dewar Designs

Orientation scattering from low temperature liquids was studied using the dewar shown in Fig. 3. This dewar has been designed for use in making Brillouin measurements also. Its size has been chosen so that scattered light in the backward direction may be collected from a large solid angle. The Brillouin shift varies very slowly as a function of angle near a scattering angle of 180° so that accurate measurements of the Brillouin shifts may be made while collecting a large cone of scattered light in this direction. By positioning the sample cell at a small solid angle with respect to the incident beam, reflected light from the dewar windows can be directed away from the optics collecting the light scattered in the backward direction. The windows on the dewar should be of fairly high optical quality to prevent light scattering. Considerable distortion existed on the outside fringes of the windows of the dewar used for orientation and Brillouin scattering measurements at low temperature. Since Brillouin and Rayleigh scattering are weak, difficulties in keeping scattered light out of the detection system ensued, especially in the backward direction. It would probably be better to antireflection coat the windows on the dewar if possible.

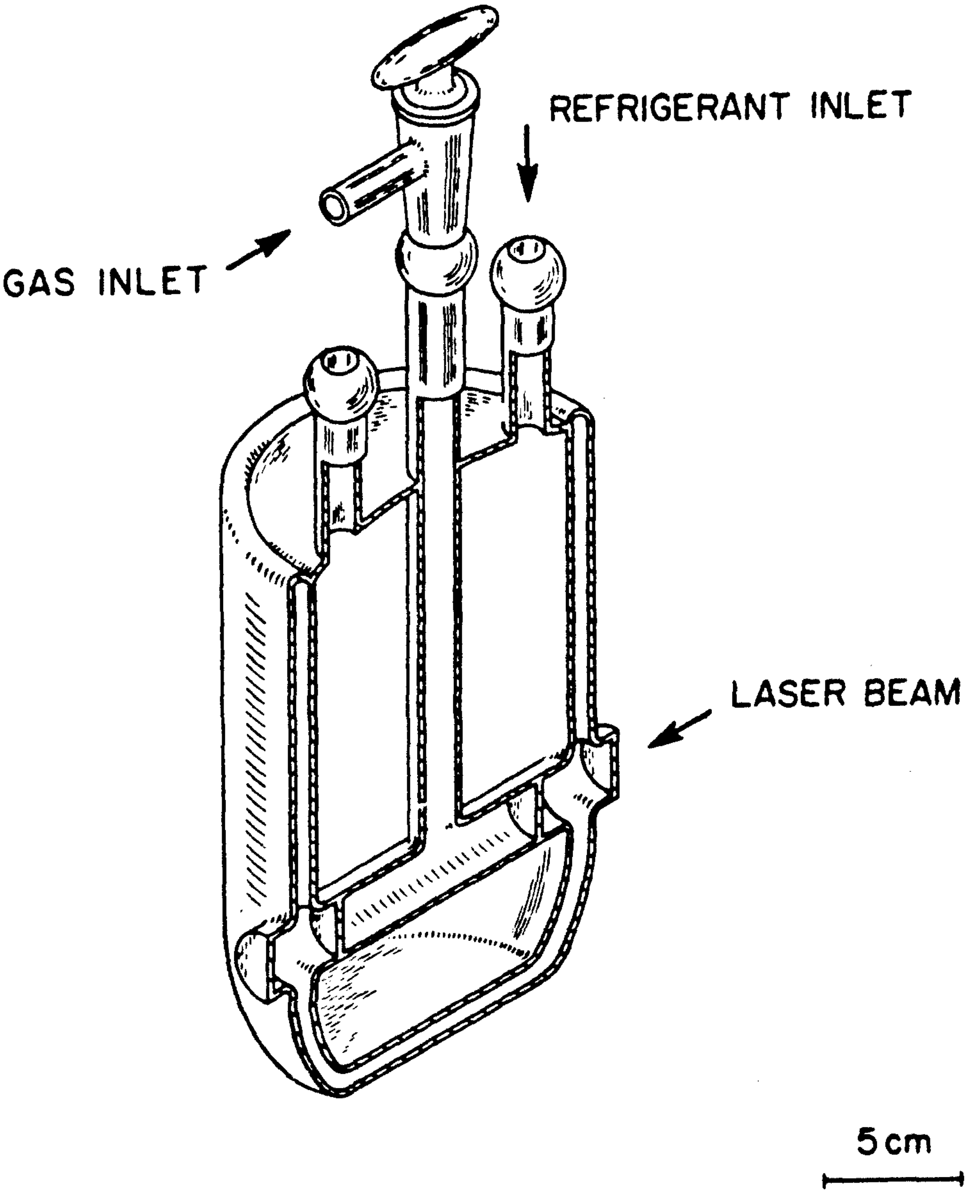


Fig. 3. Dewar for studies of orientation scattering in liquid oxygen.

Samples of liquid and solid carbon monoxide and nitrogen were grown in another dewar which had a similar design to a dewar depicted by Bass and Broida.[60] This dewar is built from quartz and has windows which are only slightly distorted. Its principal use is for Raman scattering in small liquid and solid samples (~1 cm^3) where the Raman lines are far removed from the incident line. If Raman lines are close to the incident line (such as lattice vibrations), high quality optical windows on the dewar become very important. A double monochromator[61] would probably be an aid for investigating Raman lines which are close to the incident exciting line, especially if much Rayleigh or Tyndall scattering or reflected light from the incident beam enters the spectrometer. An important design consideration in both dewars used for measurements at low temperatures was that they both have only four windows in order to cut down scattered light.

2.3 Spectroscopic Apparatus and Techniques for Obtaining Raman Spectra

Spectra were obtained photoelectrically and photographically. The principal photoelectric instrument used for recording of Raman spectra was a Fastie-Ebert[62] monochromator. This instrument was used to study orientation scattering in liquid carbon disulfide and oxygen and for obtaining Raman spectra in liquid and solid nitrogen and carbon monoxide. The monochromator is a 0.8 meter, f/10 scanning instrument which is equipped with a grating which is 75 mm long and 70 mm wide with 1200 lines/mm ruled along the length and is blazed at

5000Å in the first order. For the study of orientation scattering slit sizes of 10 and 20 microns were used, and resolutions in the neighborhood of 40000 were obtained in the first order. For Raman spectra slit sizes of 200 microns were used in a double pass Fastie-Ebert monochromator which could resolve 1Å at 5000Å or about 4 cm^{-1}. The spectra were recorded photoelectrically by using an RCA 1P28 photomultiplier whose signal was fed into a Keithley 417 picoammeter and then into a recorder with a response time of 0.25 sec.

Photographic Raman spectra were obtained in the first order using a fast (f/1.5) Bass-Kessler[63] spectrograph. This instrument contains a grating which is 13 cm long and 11 cm wide with 600 lines/mm ruled along its length. Its resolution with a 100 μ slit is 2Å in the first order. An Exakta camera was used to photograph the spectra on Kodak 103AF film.

Comparison spectra were obtained photoelectrically by placing an argon or mercury pen lamp behind the sample and putting in filters to reduce intensities of the comparison lines so that they are comparable to the Raman lines. Thus a comparison line was found 10Å away from the position of the vibrational Raman line in liquid and solid nitrogen, and in liquid and solid carbon monoxide a line was found 12Å away from the Raman lines. Photographic comparison spectra were obtained by using a mercury source or the Ar^+ laser lines themselves.

Because of the collimation of the laser beam, experimental arrangements for obtaining Raman spectra are simplified. The experimental geometry is less complicated, and polarization measurements may be made accurately as the beam may be easily polarized.

Some photographic techniques for obtaining Raman spectra in liquids are demonstrated in Fig. 4. The spectrum in Fig. 4a was taken with a laser output power of a few milliwatts passing through liquid CCl_4. Scattered light at 90° was focused with a lens on to a Bass-Kessler (f/1.5) spectrograph. A single mirror was used to reflect the beam back through the liquid, but split images arose because the reflected beam did not pass directly back upon the incident beam. The exposure time was forty minutes.

In Fig. 4b the beam was focused with a lens onto liquid CS_2. The advantage of focusing the beam through the liquid is that the image of the beam on the spectrograph will become very small so that instead of the intensity images being lines on the film, they are dots so that exposure times are reduced. The laser output was the same for Fig. 4a and Fig. 4b, but the exposure time in Fig. 4b is only three minutes. (The Raman lines of CS_2 and CCl_4 have comparable intensities). With an output power of only a few milliwatts at 4880Å stronger Raman lines may be obtained in seconds. If the laser is operated at 100 milliwatts, the exposure times for Raman spectra in organic liquids become very small.

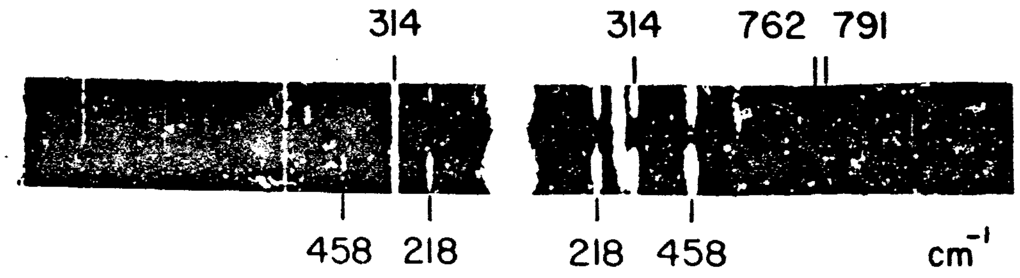
There are many methods of shortening the exposure time. A gain of nearly a factor of two may be obtained by placing a spherical mirror at 90° with respect to the incident beam and positioning it to reflect light into the monochromator. Exposure times may be decreased by a factor of about eight if one has a good sample cell so the beam may be resonated with the laser cavity. If one has an excellent sample cell, it may be placed inside the laser cavity where the beam is much more intense. Such a cell should have Brewster windows to cut down reflective losses.

Many of the techniques which are used to shorten exposure times for photographic Raman spectra may also be used to increase the photoelectric recorded intensity. There is in fact an advantage to focusing the beam in the liquid. If the beam is focussed with a lens down to a size of 20 microns, a value easily obtainable with commercial lenses, then the image of the beam may be reoriented so that it lies along the slit of the monochromator so that much more light is collected. Although Fastie-Ebert monochromators have curved slits, a gain in intensity of at least five is obtained by using a dove prism to reorient the image on the slit. If the monochromator has straight slits, one should be able to focus the beam down to 20 microns and use 20 micron slits to collect a large portion of the scattered light.

The Raman spectrum of CCl_4 obtained photoelectrically with a two passes of the beam through the liquid is shown in Fig. 5. The intensity of the laser fluctuated during this particular run but high power lasers can have stable outputs which fluctuate less than 0.1%. Our laser intensity can be made to fluctuate less than 1%. Half widths of all the CCl_4 Raman lines are much broader than the laser line. The Raman line at 458 cm^{-1} in CCl_4 is shown in Fig. 6. It has a halfwidth of about 11 cm^{-1} and is asymmetric.

The experimental arrangement for obtaining Raman spectra in liquid and solid carbon monoxide and nitrogen is shown in Fig. 7. Lenses which focus the light on the monochromator are chosen to fill the instrument.

a, RAMAN SPECTRUM OF CCl_4



b, RAMAN SPECTRUM OF CS_2

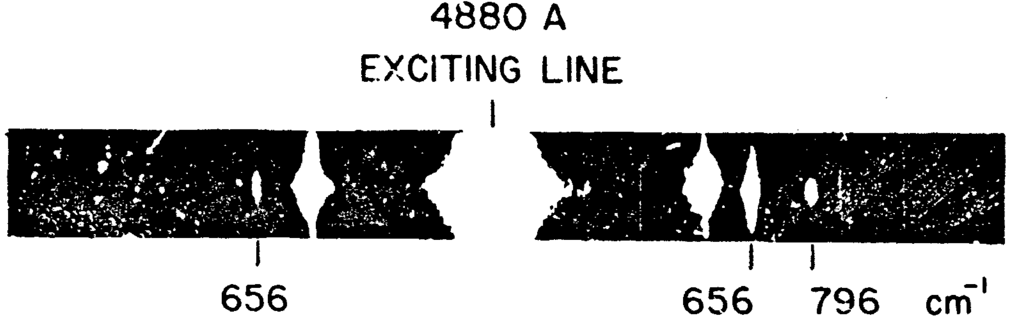


Fig. 4.

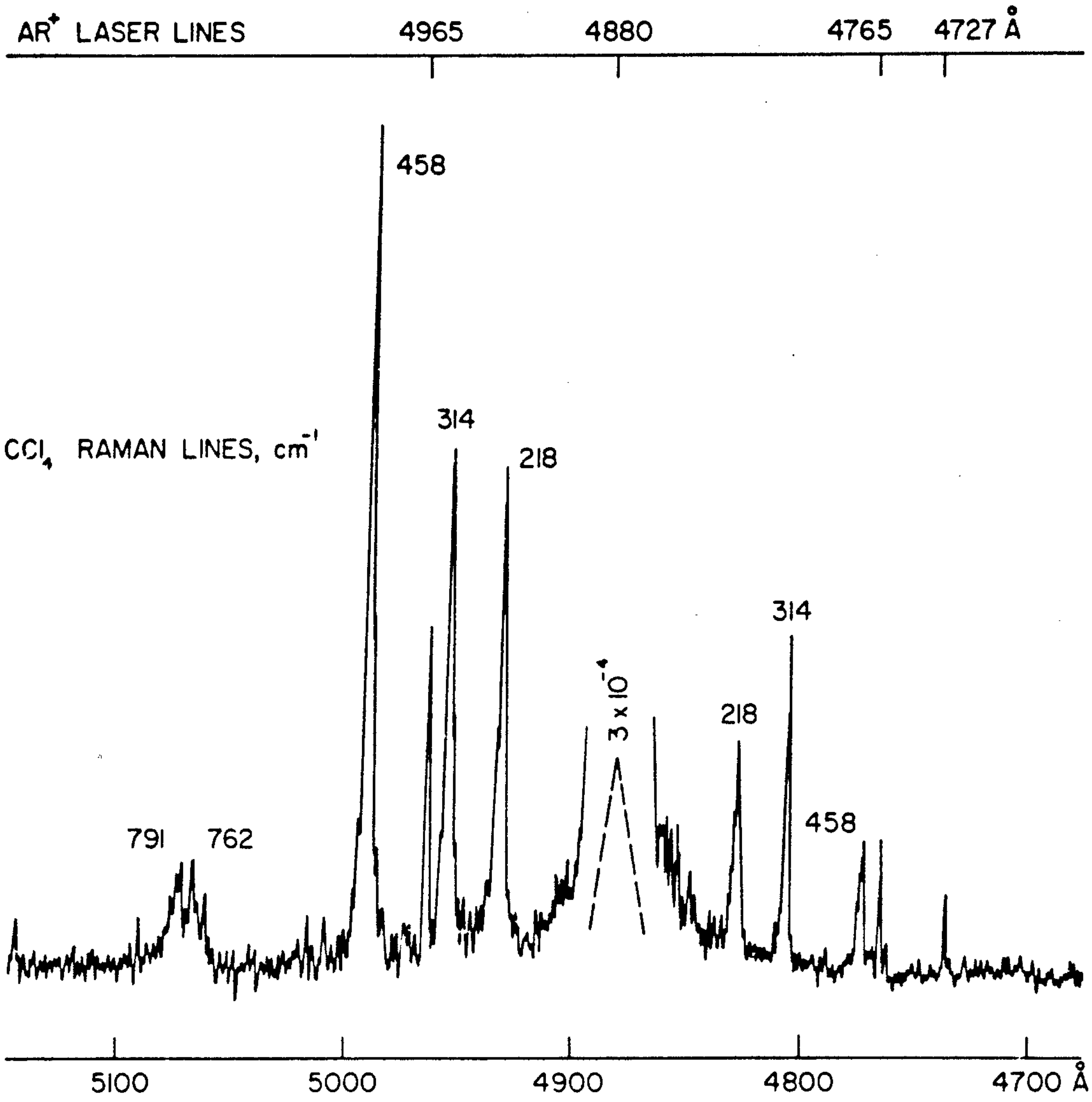


Fig. 5. Photoelectric trace of Raman spectra of CCl_4.

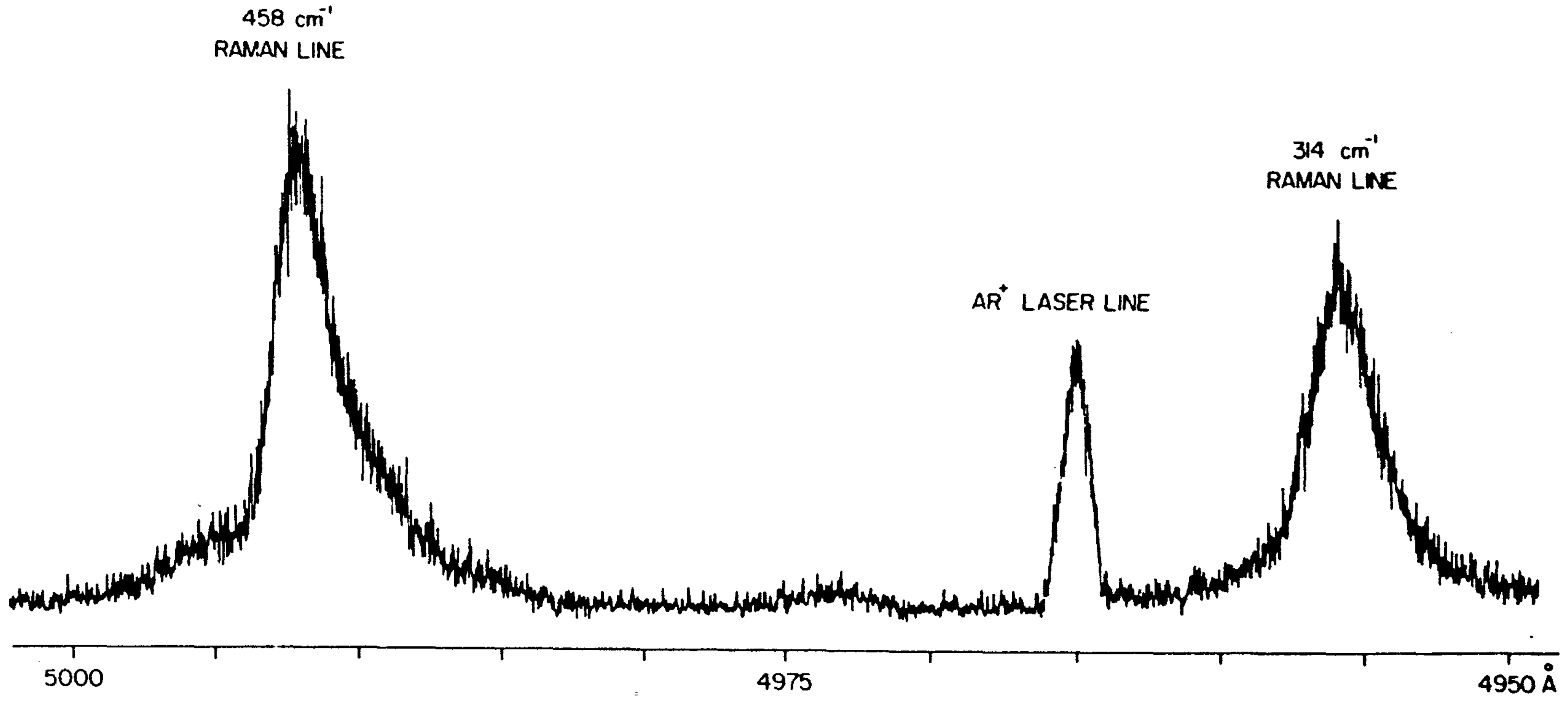


Fig. 6. The 314 cm^{-1} and 458 cm^{-1} Raman lines of CCl_4.

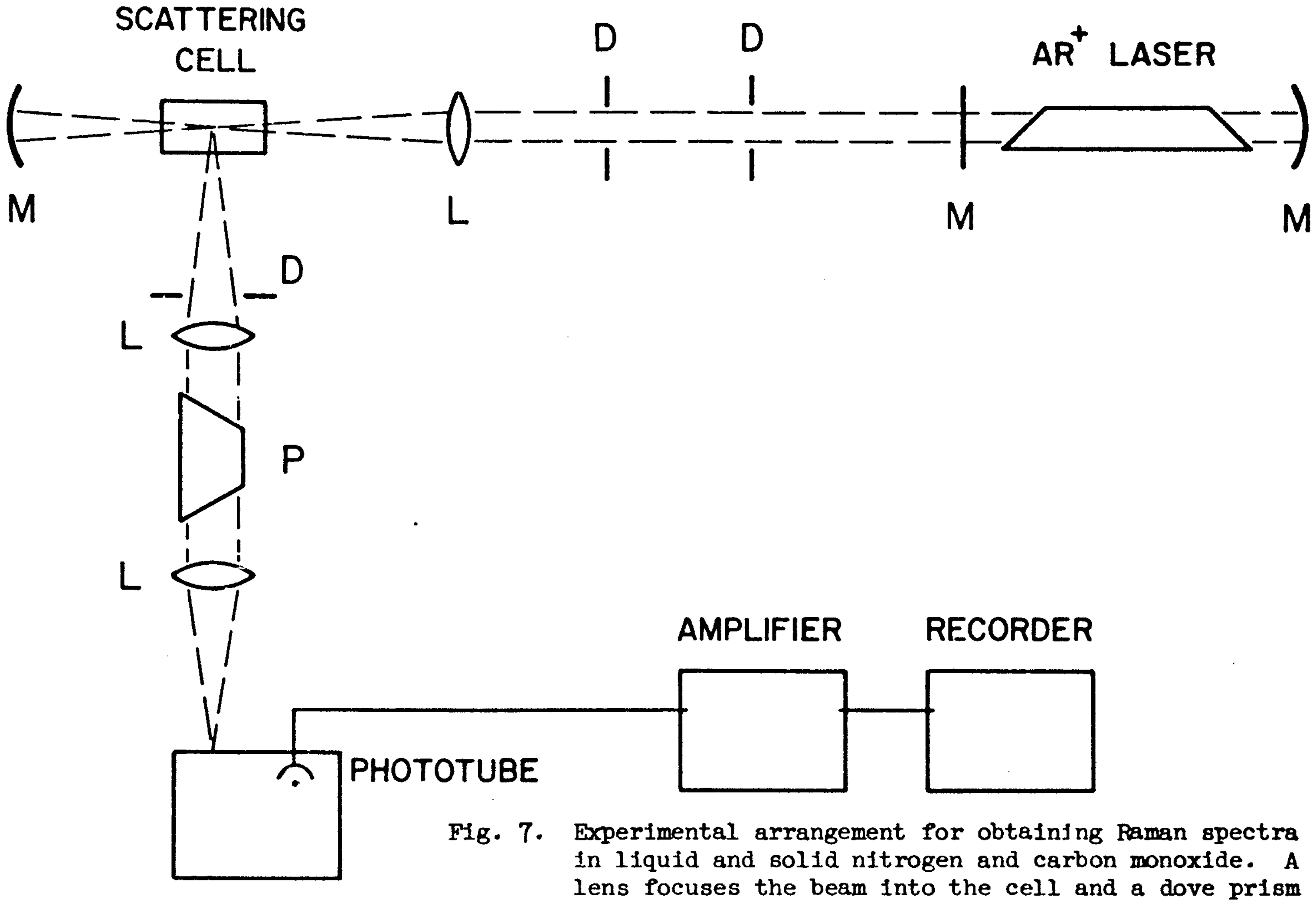


Fig. 7. Experimental arrangement for obtaining Raman spectra in liquid and solid nitrogen and carbon monoxide. A lens focuses the beam into the cell and a dove prism is used to reorient the image on the slit of a Fastie-Ebert monochromator: D, diaphragm; M, mirrors; L, lenses, P, dove prism.

III. EXPERIMENTAL RESULTS

3.1 Light Scattering from Orienting CS_2 Molecules

Orientation scattering by CS_2 molecules in pure CS_2 and mixtures of CS_2 and CCl_4 was studied in order to learn about molecular motion and structures in the liquid. Measurements of lineshapes, halfwidths, and depolarization of orientation scattering were made toward this end. In addition, intensities of the Rayleigh and Brillouin components were measured relative to the orientation scattering.

Experimental results are described in detail in Appendix I and will be briefly summarized here. Results are all obtained with the experimentally popular case of the incident light polarized perpendicular to the plane of scattering with the scattered light detected at 90°. The scattered light is passed through an analyzer which can be positioned so that light with the wave vector perpendicular and parallel to the plane of scattering can be studied.

Lineshape of the Orientation Scattering

The lineshape of the orientation scattering in CS_2 was found to be nearly Lorentzian. The spectra have long tails characteristic of the Lorentzian as opposed to the Gaussian shape. There is some deviation from the Lorentzian shape throughout the spectrum. The deviation becomes large at frequency shifts of 50 to 60 cm^{-1} where the intensity increases markedly over a Lorentzian distribution. In liquid mixtures the lineshapes deviate further from Lorentzian shapes. However, the long tail characteristic of Lorentzian lineshapes still persists in mixtures.

Intensities of the Orientation Scattering

The intensity of the orientation scattering stays fairly constant as a function of temperature in pure CS_2. The intensity of the orientation scattering is very strong in CS_2 as compared to such liquids as benzene, toluene, and nitrogen. This is undoubtedly due to the fact that CS_2 is a highly anisotropic molecule.

In liquid mixtures of CS_2 and CCl_4 the intensity drops as more CCl_4 is added. The intensity of light scattered from the mixture is not proportional to the number of CS_2 molecules in the mixture. The effective scattering cross section of a CS_2 molecule seems to drop as the CCl_4 concentration increases. The intensity at zero frequency shift is proportional to the CS_2 concentration, however.

Halfwidths of the Scattered Radiation

The halfwidths of the orientation scattering were measured in pure CS_2 from the triple point at $161^{\circ}K$ to near the boiling point at $313^{\circ}K$. Halfwidths ranged from less than 0.1 cm^{-1} near the triple point up to about 6 cm^{-1} near the boiling point. Measured halfwidths were approximately proportional to T/η and to $T - T_p$ where T is the temperature, T_p is the triple-point temperature, and η is the viscosity.

In CS_2-CCl_4 mixtures halfwidths measured at room temperature in the mixture were approximately proportional to $1/\eta$.

Depolarization Measurements and Ratios of Intensities of the Rayleigh and Brillouin Components to Orientation Scattering

Depolarization measurements in CS_2 at room temperature show that the ratio of the scattered light with electric field vector perpendicular to the plane of scattering to that parallel to the plane of scattering is approximately 3/4 for the orientation scattering. The intensity of the Rayleigh line plus the two Brillouin components is about 0.47 that of the orientation scattering at room temperature. In mixtures of CS_2 and CCl_4 this ratio rapidly increases as more CCl_4 is added. In a mixture containing 10% CS_2 by volume this ratio is approximately 12.5.

3.2 Vibration-Rotation Spectra of Liquid Oxygen

In liquid oxygen the Raman line appears to be composed of two parts - a sharp polarized line at the vibrational frequency and a broad depolarized rotational wing. The Raman line at 1552 cm^{-1} was studied as a function of temperature from $64^\circ K$ to $90^\circ K$. A value of the relaxation time for the rotating molecules was calculated from the slope of the plot of the inverse intensity vs the square of the frequency shift of the scattered light. This method of analysis was chosen because the plot yielded a straight line in the wings, indicating that the distribution was Lorentzian. Also it was not obvious that the scattered light at zero frequency shift from the Raman line was due to the anisotropic scattering, even when the analyzer was positioned to pass light polarized parallel to the plane of scattering. Halfwidths may not give a true measure of the frequency broadening due to molecular rotations especially since the isotropic scattering component is very intense in liquid oxygen. Data, analyzed by plotting the inverse of the intensity vs. the frequency shift squared, show that the frequency broadening in liquid oxygen is about 48 cm^{-1} at 64°K, 47 cm^{-1} at 77°K, and 36 cm^{-1} at 90°K. These frequency broadenings correspond to relaxation times of 1.1×10^{-13} sec., 1.1×10^{-13} sec., and 1.5×10^{-13} sec., respectively. The analysis was complicated by the determination of the zero light level of the spectra because of the difficulty of eliminating scattered light. Errors in the determination of the broadening may be as much as 50%. However, it is clear that no great change in the relaxation time is found when the temperature is varied.

3.3 Molecular Crystal Growing Techniques

The method used for growing crystals was similar to the technique of Bolz, Broida and Peiser[64] and Savoie and Anderson.[65] Liquid and solid nitrogen and carbon monoxide were grown by liquifying the gas and then pumping on the refrigerant to solidify the liquid. Research grade purity nitrogen gas and 99% purity carbon monoxide gas (Matheson Co.) were used. In order to grow solid nitrogen, nitrogen gas was first condensed to a liquid by pumping on a liquid oxygen refrigerant with a forepump. Then just enough refrigerant was put in so that the level of the oxygen was about the same as the level of the liquid nitrogen. By pumping on the liquid oxygen refrigerant clear solid nitrogen could be grown when the temperature fell below $63^{\circ}K$ as measured by the vapor pressure of the refrigerant using a mercury manometer. If the refrigerant level is higher than the liquid, it was observed that the top of the liquid nitrogen freezes and vapor snakes form.[66] Even when the refrigerant level is below the nitrogen level, vapor snakes will form in the liquid nitrogen if a portion of the liquid becomes completely surrounded by solid nitrogen. However, these vapor snakes can be eliminated before they proceed very far by discontinuing the pumping on the liquid oxygen refrigerant. As soon as the vapor snakes disappear, the pumping is resumed. Often this process was repeated many times while growing a nitrogen solid. However, nitrogen solids obtained were perfectly clear without any visual imperfections. Nor could any imperfections be found when the laser beam was scanned through the sample. Using a similar technique for growing crystalline argon Bolz et al.[64] and R. F. Followell[67] showed that crystal sizes in the sample were of the order of millimeters and that larger crystal sizes were grown if the sample was cooled slowly. Samples of nitrogen were cooled quite slowly and it took one to two hours to grow the solid. Samples of liquid and solid carbon monoxide were grown in the same dewar by a similar technique. Samples of CO were quite milky because they contained some CO_2 impurity. However, upon passing the CO through a liquid oxygen trap prior to condensation in the dewar much but not all of the CO_2 was eliminated. Samples which were finally used looked slightly soapy. However, transmission of the samples was sufficient so that Raman spectra could be taken.

3.4 Raman Scattering in Liquid and Solid Nitrogen and Carbon Monoxide

Photoelectric traces of the Raman spectra of liquid and solid nitrogen are shown in Fig. 8. The spectra show that the shift of the vibrational Raman line upon going from liquid to solid is small. The position of the vibrational Raman line in both liquid and solid nitrogen was measured as 2327.5 ± 0.5 cm^{-1}. In both liquid and solid carbon monoxide the Raman line was found to be at 2138 ± 0.5 cm^{-1}. The temperature of the nitrogen solid was near $63^{\circ}K$, the triple point of nitrogen. The temperature of the liquid carbon monoxide was $81^{\circ}K$ while the temperature of the solid carbon monoxide was about $68^{\circ}K$, the triple point of carbon monoxide. Solid nitrogen and solid carbon monoxide exist in at least two phases, an alpha phase and a beta phase. Only the alpha phase was studied. In liquid carbon monoxide the Raman line consists of a polarized central part and a depolarized wing, but the intensity in the wings was too weak to measure a rotational relaxation time. Because of strong scattered light near the Rayleigh line, no information could be obtained on the Rayleigh wings or on lattice vibrations.

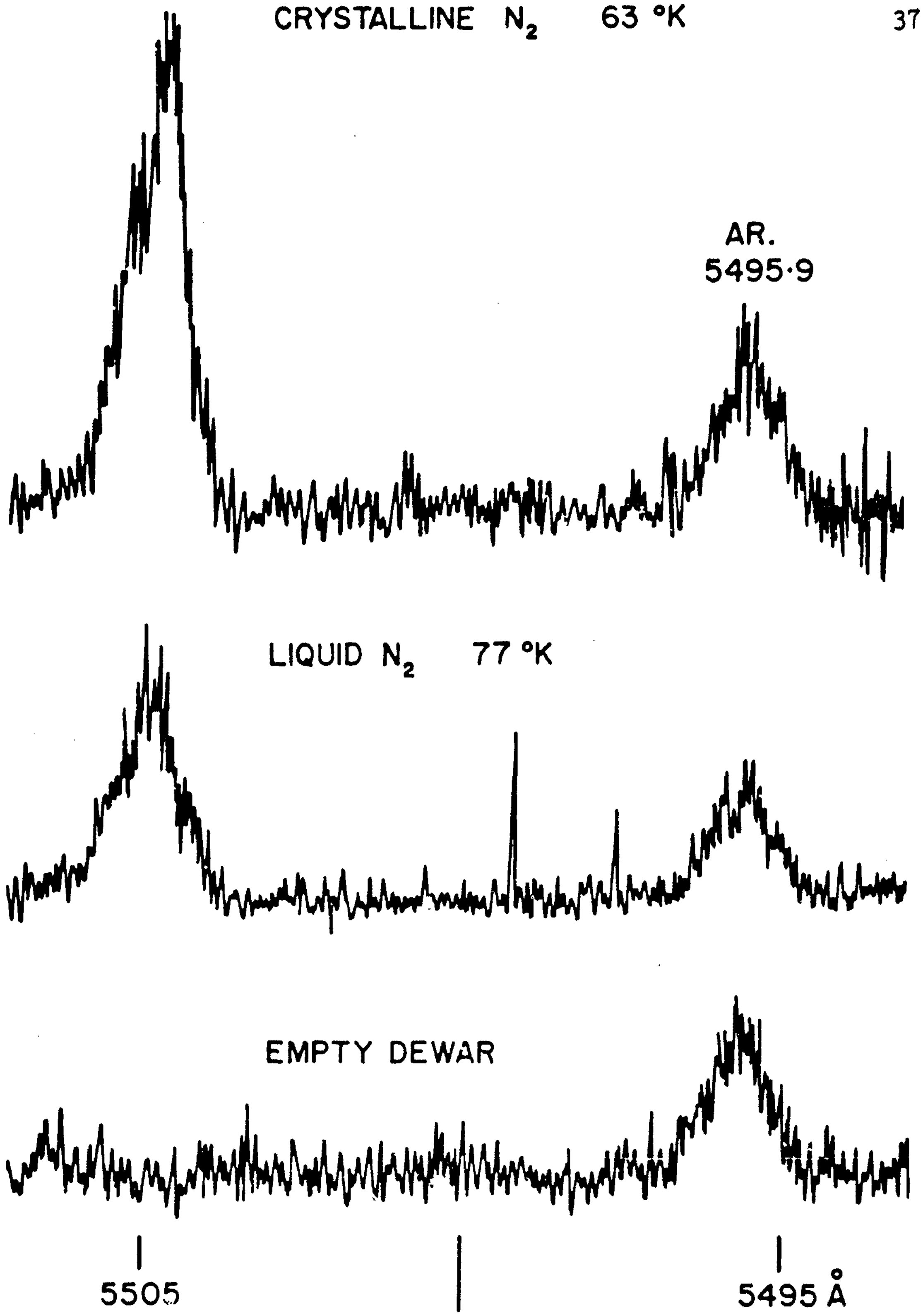


Fig. 8. Raman spectra of liquid and solid nitrogen.

IV. THEORETICAL INTERPRETATION OF RESULTS

4.1 Theoretical Interpretation of Orientation Scattering Measurements in CS_2

That the scattered radiation is approximately Lorentzian is in agreement with predictions of Leontovich[11] and of Starunov.[15] Starunov has derived formulas which indicate that the increase in the scattered radiation above the Lorentzian shape at 50 cm^{-1} may be due to quasi-crystalline lattice vibrations. In addition he has made measurements which indicate that such quasi-crystalline lattice vibrations exist in many liquids. The main reasons for attributing the increase of intensity at 50 cm^{-1} to 60 cm^{-1} to lattice vibrations in liquids are that the frequencies are close to the lattice vibrations in the crystal and that many other liquids exhibit such phenomena and their frequencies are also near the lattice vibrations in crystals. The structure in the liquid is spectrally broad and, of course, is probably very local in contrast to the long range structure in crystals. These results have obvious pertinence to the problem of determining the structure of a liquid.

Halfwidths are proportional to the temperature of the liquid divided by the viscosity of the liquid, a measurement in agreement with the predictions of the Debye theory. The Debye theory[68] predicts that the relaxation time for the rotation of molecules to be attenuated to 1/e is given by

$$\tau = 4/3\ \pi a^3 \eta / kT = \frac{V\eta}{kT} \qquad (1)$$

where the molecule is considered to be a sphere of radius a, η is the viscosity of the liquid, k is the Boltzmann constant, and T is the temperature of the liquid. Debye has made several approximations to obtain this simple formula. A molecule is normally not spherical in shape, so for greater accuracy one should describe the motion of the molecules in terms of three relaxation times corresponding to molecular rotation about the three principal axes. Also viscosity has to do with a linear exchange in momentum and is not necessarily the same as angular viscosity. Molecules also may make very large rotations without collisions so that one must be very careful in applying the Debye equation under certain conditions. At any rate experiment indicates that in CS_2 the Debye equation is a very good approximation. This is in part because CS_2 is a fairly large and symmetric molecule with a large moment of inertia.

In liquid mixtures halfwidths are approximately proportional to the temperature divided by the viscosity of the liquid which agrees with the Debye theory. Some deviation from the Debye theory was noticed, but this seems to be due to local field corrections and the different shapes of the two molecules. Thus the total intensity scattered by an individual CS_2 molecule decreases as more and more CCl_4 is added. But local field corrections predict that the intensity should decrease when more CCl_4 is less than that of CS_2. Furthermore using a simple approximation given by Eckhardt and Wagner[69] for Raman scattering, that the intensity goes as $(n^2 + 2)^4$, where n is the index of refraction of the medium, shows that the decrease in intensity is in agreement with theory except at very low CS_2 concentrations. At very low CS_2 concentrations not all of the scattering is due to the CS_2 since there appears to be some residual scattering from CCl_4. The scattering from CCl_4 may be due to deformations of the molecule during collisions or to some isotopic effect. Rank has also reported some depolarized light scattered by CCl_4.[29]

Since the Debye relation appears to hold in CS_2, a measurement of the interaction volume of the molecule may be made according to equation 1. Such a measurement yields an interaction volume for CS_2 of 20.7×10^{-24} cm^3. Conversely a knowledge of the interaction volume allows a measurement of the viscosity of the liquid. This is most useful for this is a very simple means of measuring viscosity. The viscosity of CS_2 below 260°K has not been measured. Using equation 1 viscosity values of 0.79 cp were found at 210°K, 0.60 cp at 230°K and 0.50 cp at 250°K.

Depolarization measurements of the orientation scattering in CS_2 agree with theoretical predictions of Leontovich[11] and Starunov[15] who both predict that the ratio of the intensity of the light scattered with electric field vector perpendicular to the plane of scattering to that scattered parallel to the plane of scattering should be 3/4. According to Pecora and Steele,[39] depolarization measurements can yield information on angular correlations between molecules in liquids. By assuming that the total intermolecular interaction energy of the fluid is given by the sum of molecular pairwise potential energies, and adopting a rotational Brownian motion model, Pecora and

Steele have solved the problem of inelastic scattering of light by aspherical molecules in liquids. Steele[70] has analyzed the equations for the experimental case where the beam is polarized perpendicular to the plane of scattering, the scattering angle is 90°, and the analyzer is positioned perpendicular and parallel to the plane of scattering. Since this experimental arrangement is identical to our arrangement, Steele's equations may be used. For CS_2 the equation which relates the depolarization to the angular correlation takes on a particularly simple form. This is because CS_2 has two polarizabilities which are the same, and because the shift due to translational motion in CS_2 is of the order of $0.15\ \mathrm{cm}^{-1}$ which is much less than the width due to the rotational motion which is about $5\ \mathrm{cm}^{-1}$. The equation of interest here is[70]

$$\frac{I_{A||}}{I_C + 2I_B} = \frac{\alpha_2^2}{\alpha_0^2} \cdot \frac{1 + \rho\langle \frac{3}{2}\cos^2\theta_{12} - \frac{1}{2}\rangle}{15\,\rho\,\kappa_T\,kT} \qquad (2)$$

where $\alpha_2 = \alpha_z - \alpha_x$ where α_z is the polarizability along the internuclear axis of the molecule and α_x is the polarizability perpendicular to the internuclear axis, $\alpha_0 = (\alpha_x + \alpha_y + \alpha_z)/3$, $I_{A||}$ is the intensity of the orientation scattering with electric field vector parallel to the plane of scattering, $I_C + 2I_B$ is the intensity of the central component plus the intensity of the two Brillouin components, ρ is the number density of molecules in the liquid, κ_T is the isothermal compressibility, k is Boltzmann's constant, T is the temperature, and θ_{12} is the angle two molecules make with respect to one another when the two are moved together so that their centers coincide.

According to equation 2 a determination of the relative intensities of the Rayleigh and Brillouin components to that of the orientation scattering provides a way of measuring angular correlations between molecules in liquids. From data in Table I of Appendix I the ratio of $I_{A||}/(I_C + 2I_B)$ for CS_2 at 20°C is 0.91. Using equation 2, a value of 0.42 was calculated for the quantity $1 + \rho<3/2 \cos^2\theta_{12} - 1/2>$. The quantity $\rho<3/2 \cos^2\theta_{12} - 1/2>$ may be interpreted as the number of molecules with a particular value of θ_{12} multiplied by $3/2 \cos^2\theta_{12} - 1/2$ summed over all of the molecules. It seems physically plausible to assume that nearest neighbors to a central molecule are more effective in aligning with a central molecule. Thus in CS_2 it is assumed that the 12 nearest neighbors are responsible for the contribution to $\rho<3/2 \cos^2\theta_{12} - 1/2>$. The quantity $<3/2 \cos^2\theta_{12} - 1/2>$ is considered to be zero outside this inner shell of molecules. But from experimental measurement it has been found that $< 3/2 \cos^2\theta_{12} - 1/2>$ is equal to -0.58 in CS_2. This implies angular correlations between CS_2 molecules exist in the liquid. Furthermore perpendicular orientations of CS_2 molecules are favored over parallel orientations of the internuclear axis. This is because $<3/2 \cos^2\theta_{12} - 1/2>$ becomes negative when θ_{12} exceeds 54°. It appears that a measurement of the ratio of the Rayleigh and Brillouin intensities to that of the orientation scattering provides a simple method for determining angular correlations between molecules in liquids.

4.2 Theoretical Interpretation of the Vibration-Rotation Spectra of Liquid Oxygen

In liquid oxygen the scattering at the vibrational Raman line may be separated into an isotropic and an anisotropic part. The anisotropic part has to do with molecular rotations. Using Debye's equation 1, substituting values for the viscosity from the NBS low temperature tables,[71] and approximating the molecular radius by the radius obtained from the rotational shift in a gas, results in the prediction that the frequency broadening of the depolarized light in liquid oxygen should decrease from 38 cm^{-1} at 90°K to about 5 cm^{-1} at 54°K. The reason for this large change in the frequency broadening predicted by Debye is that the viscosity increases quite markedly at lower temperatures and also there are less collisions at lower temperatures. However, experimental measurements indicate that the Debye theory is inapplicable in liquid oxygen. The Debye theory does predict the right magnitude for the frequency broadening but fails to predict the correct temperature dependence. The reason that the Debye theory does not predict the correct temperature dependence may be because the collision time is the same order of magnitude as the time for a complete rotation of the molecule. In liquid carbon disulfide this was not true as the moment of inertia of the carbon disulfide molecule is large and the measurements were made at much higher temperatures. However, even in carbon disulfide it is not correct to strictly describe the process in terms of small angular rotations.

Results in liquid oxygen are more easily explained in terms of the theories of Frenkel[72] and Eyring.[73] Their approach is to represent the thermal motion of the molecules by infrequent transitions from one equilibrium position to another. Motions of molecules are described in terms of thermal vibrations or of rotational oscillations between these transitions. The mean lifetime of a molecule in an equilibrium position is largely dependent on the form of the intermolecular potential function and on the temperature. Frenkel and Eyring have derived a relationship between viscosity and the height of the potential barrier which a molecule has to climb over to get from one transition position to another. This relation is

$$\eta = Ce^{U_1/kT} \tag{3}$$

where η is the viscosity, U_1 is the potential barrier, and C is a constant.

Experimental measurements by A. V. Rakov[74] show that the temperature dependence of the depolarized line can be put in the form

$$\Delta\omega = \Delta(1/\tau) = B\ e^{-U/kT} \tag{4}$$

where U is the potential barrier for the rotation of a molecule in the liquid, and τ is the mean time for reorientation of the molecule.

Vuks[75] has found that $U = U_1$ in most liquids. That is barriers which are calculated from viscosity data agree with those obtained from the orientation scattering.

One way of interpreting the experimental results on the orientation scattering in liquid oxygen is that the potential barrier for rotation of the molecules is very small because of the size and shape of the oxygen molecules. If the potential barrier for reorientation is small, Frenkel's theory predicts that the viscosity for rotation will be small. That is if $U << kT$, then one would not expect the broadening to change very much with changing temperature. In fact the conclusion is that U is much less than kT in liquid oxygen so that the molecules essentially rotate freely. This conclusion is in agreement with results of Crawford et al.[76]

4.3 Raman Spectra of Liquid and Solid Nitrogen and Carbon Monoxide

The Raman lines in liquid and solid nitrogen and carbon monoxide are shifted only slightly from that of the gas. The Raman line in gaseous nitrogen has been found to be at 2331 cm^{-1},[77] while the Raman line in gaseous carbon monoxide has been reported at 2139 cm^{-1},[78] and 2145 cm^{-1}.[79] Thus the vibrational frequency of the molecules appears to be a few cm^{-1} less in the liquid and solid than that of the gas. The lines in the liquid and the solid have been found within experimental accuracy to be in the same position for both N_2 and CO. It is not surprising that CO and N_2 behave so similarly in the solid and liquid as the molecules are about the same size and weight. Since the liquid and solid Raman lines are in the "same" position, it may be concluded that the ground state structure is modified very little by the structure of the medium. Similar results have been found for CO in infrared studies. Thus Ewing[80] finds that the fundamental vibration of $C^{12}O^{16}$ is at 2139 cm^{-1} or shifted about 4 cm^{-1} below the gas and that the band center does not shift upon going to the solid.

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APPENDIX I

NOT INCLUDED

Light Scattering from Fluctuations in Orientations of CS_2 in Liquids

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Phys. Rev., to be published

APPENDIX II

NOT INCLUDED

Brillouin Scattering in Liquids at 4880A

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Proc. IEEE, J. Quant. Elec. 2, 89(1966).

APPENDIX III

Brillouin Scattering in Liquid NH_3 and ND_3

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and S. L. Shapiro, unpublished

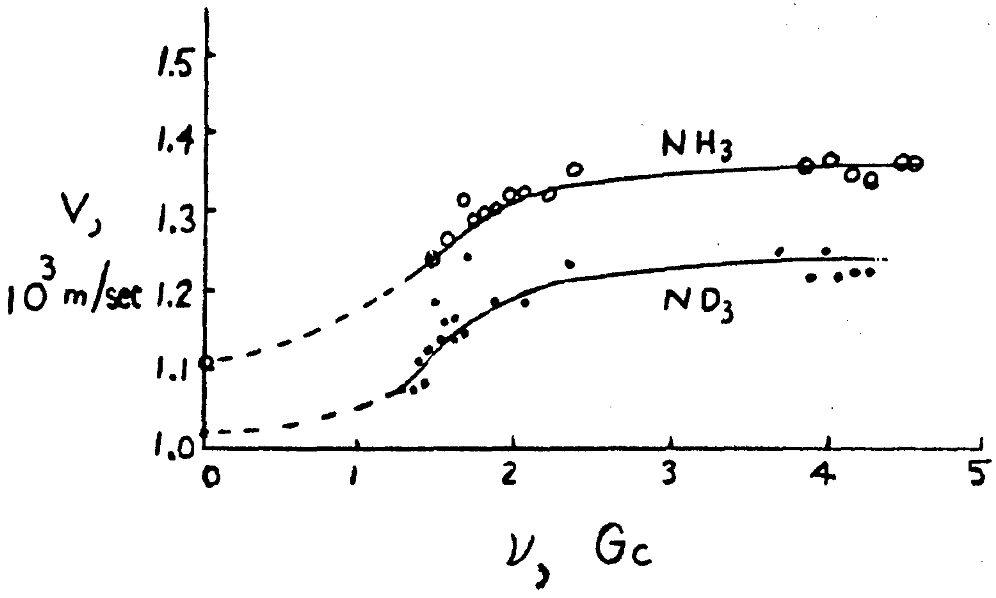
APPENDIX III

Brillouin Scattering in Liquid NH_3 and ND_3

A He^3-Ne laser at 6328A was used to observe Brillouin Scattering in liquid NH_3 and ND_3. The Brillouin lines were resolved from the Rayleigh line with a Fabry Perot interferometer. The acoustic dispersion curve of the velocity of the sound waves vs their frequency was obtained by measuring the Brillouin shifts and using the equation[1] $\Delta\nu = \frac{2nv}{c}\nu_o \sin(\theta/2)$ to calculate the velocity of the phonons. In this equation n is index of refraction, $\Delta\nu$ the Brillouin shift, ν_o the frequency of the incident light beam, θ the angle of scattering, and v the velocity of the phonon.

The Fabry Perot interferometer was mounted on a table which revolved about the sample. Fringe patterns were photographed on Polaroid 3000 speed film, exposure times being about five minutes. This exposure time was for a laser output of 35 milliwatts and Fabry Perot flats of 2 inches in diameter, $\lambda/100$ flatness, and 85% reflectivity. The sample cell was spherical and the angle was collimated so that only a few degrees of solid angle were photographed at one time. In this manner the acoustic dispersion curve was measured from angles of 28° to 150°. The accuracy of the measurements was about 4%. It is difficult to obtain higher accuracy by using photographic techniques so that when higher accuracy is desired, photoelectric scanning should be used to record the fringes.

As shown in the figure below, a large velocity dispersion was detected in both NH_3 and ND_3.

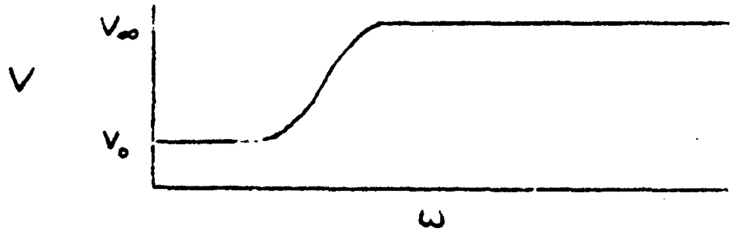


Values for the velocity of sound below 1.2 Gc were calculated from a semiempirical formula due to Schaafs. The dispersion in the velocity of sound in liquid NH_3 and ND_3 is about 20% over the range measured. All measurements were made at room temperature (21°C).

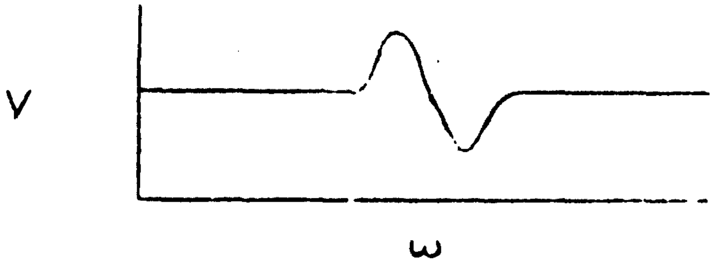
Velocity dispersions exist in liquids because of transfer of energy from translational modes in the liquid to vibrational and rotational modes of the molecules or because short range structure exists in some liquids, associative liquids, and structural changes may lead to an increased absorption of the sound waves. An equation has been derived which describes the velocity dispersion for either process as[2]

$$v_0^2/v^2 = 1 - \left(\frac{v_\infty^2 - v_0^2}{v_\infty^2}\right) \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \tag{1}$$

where v is the velocity of the sound wave, v_0 is the velocity at zero frequency, v_∞ is the velocity at infinite frequency, ω is the frequency of the sound wave, and τ is the relaxation time. This equation is for a single relaxation process and the velocity as a function of frequency then looks like this



Another possibility for absorption of sound waves is a resonance phenomena. That is when a sound wave has the same frequency as another mode in the system and the coupling between the two modes is large enough then a large absorption could take place at the resonance frequency. Such a mode might be a low lying optical mode in a molecule. The solution for the velocity of sound as a function of frequency would then look something like the solution of the damped harmonic oscillator. Such a velocity dispersion looks like this



At any rate the velocity decreases as the frequency approaches the resonance frequency.

Using equation 1 the curves yield a relaxation time of 1.6×10^{-10} sec. for NH_3 and 1.3×10^{-10} sec. for ND_3. A measurement of the relaxation time does not tell one what the mechanism is for the relaxation. One would have to do a theoretical calculation to show which relaxation mechanism dominates. There are two possible mechanisms for the relaxation in NH_3. Either a structural relaxation or a thermal relaxation is possible. A structural relaxation may appear in liquid NH_3 for the same reason it appears in water. Both the water molecule and the ammonia molecule possess dipole moments. Molecular sizes and dipole moments are similar in NH_3 and H_2O.

The other possible relaxation mechanism is the relaxation of the sound wave to vibrational and rotational modes of molecules. Both the thermal and the structural mechanisms could possibly play a role in NH_3. One can calculate the strength of the polar bonds in an associative liquid by different methods. M. McClintock[3] has calculated that the energy of interaction between adjacent molecules in NH_3 is weaker than in water. His rough calculation shows that the interaction energy is about four times weaker in NH_3 than water. However, as pointed out by Herzfeld and Litovitz, associative liquids have similar properties as water and because they behave very much like water it is quite plausible to assume that if the structural mechanism is the cause of the excess absorption in water it probably is the cause in all associated liquids.[4] In liquid ND_3 there is another interesting possibility. The velocity dispersion could come about because of the resonant interaction of a sound wave with the inversion vibration of ND_3. The inversion frequency in NH_3 gas is very high and cannot be reached by acoustic waves which couple to light at 6328Å. But in ND_3 the inversion vibration in the gas occurs at 1.6 Gc. As a resonant interaction would result in a decrease in velocity in the velocity vs. frequency curve, and since this was not observed to within the experimental error, it seems unlikely that a resonant interaction plays a role.

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