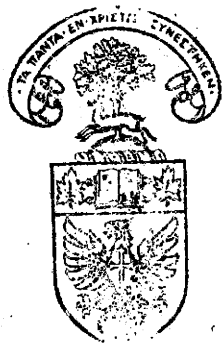


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INDUCED ANISOTROPY
IN LIQUIDS

by

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A Thesis

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ABSTRACT

The spectra of depolarized light scattered from isotropic and anisotropic liquids were investigated in order to obtain information on both the reorientational and collisional motions of the liquid molecules.

The liquid spectra taken at 22°C on a Coderg spectrometer (1 cm.⁻¹ slits) were decomposed into relaxational and collisional components using least squares fitting techniques. Integrated intensities and depolarization ratios in the zero cm⁻¹ (1 cm⁻¹ = 3 x 10¹⁰ hz.) frequency shift region as well as in the >5 cm⁻¹ region are reported.

The isotropic liquid spectra from 5 cm⁻¹ consisted of a narrow Lorentz and a broader collisional component which was exponential at shifts > 10 cm⁻¹. The anisotropic spectra also consisted of relaxational and collisional components; however, the integrated intensity of the relaxational and the collisional components increased by a factor of 20 and 10 respectively from the isotropic liquids.

A simple model based on frame distortion induced anisotropy was constructed to predict the relative intensity ratios of the collisional component for both isotropic and anisotropic liquids.

The relaxation time of the Lorentz component was interpreted for both isotropic and anisotropic liquids as being the average time between collisions. It was found to vary as $\mu^{3/2}/\rho$, where μ is the reduced mass of two colliding molecules and ρ the liquid density.

The line width parameter $1/\nu_0$ for all the collisional components was interpreted as being a measure of the duration of a collision and was found to vary as $\mu^{1/2}$ independent of the density ρ .

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CHAPTER I

INTRODUCTION

Light scattering has become an extremely useful method of investigating both reorientational⁽¹⁾ and collisional⁽²⁾ motions of molecules in liquids.

The spectrum of visible light scattered by a liquid generally consists of a Rayleigh line⁽³⁾ (due to fluctuations in the dielectric constant), a Brillouin doublet⁽⁴⁾ (due to scattering from longitudinal phonons), and a broader depolarized line⁽⁵⁾ associated with the anisotropic molecular polarizability.

Heterodyne or beat frequency techniques with a resolution of 10^{14} have been used to investigate Rayleigh scattering due to density and orientational fluctuations in macromolecules⁽⁶⁾ and liquid crystals⁽⁷⁾. Diffusion constants, Doppler velocities (typical range of 10^{-5} m/s to 10^2 m/s), and molecular orientation times (10^{-3} to 10^{-4} sec.) can be determined in this manner.

For many liquids the depolarized line can be resolved by scanning Fabry-Perot methods⁽⁸⁾ with a resolution of about 10^6 . The spectral profile is Lorentzian, with the linewidth parameter representing the relaxation time of fluctuations in the molecular motion⁽⁹⁾. Recently, G. Stegeman and B. P. Stoicheff have showed that liquids composed of anisotropic molecules exhibit a narrow depolarized doublet, superimposed

on the depolarized Rayleigh line⁽¹⁰⁾. This doublet is believed to originate from scattering from transverse shear waves.

For low viscosity anisotropic liquids, the depolarized line can be resolved by conventional spectrometers with a resolution of 10^4 (11).

Liquids composed of spherical-top molecules have isotropic polarizabilities and do not exhibit the narrow Lorentz due to orientation scattering; however, depolarized scattering can result from an induced anisotropy produced when pairs of atoms or molecules collide⁽¹²⁾. The spectrum is a broad ($>10 \text{ cm}^{-1}$) exponential and occurs in all liquids, although weaker than orientation effects in the anisotropic liquids. The depolarized spectra of the isotropic molecules show an increased intensity in the low frequency ($\nu < 15 \text{ cm}^{-1}$) region⁽¹³⁾, which is believed to be due to intercollisional interference effects⁽¹⁴⁾.

It is the purpose of this project to study the depolarized spectra of isotropic and anisotropic liquids, starting from a frequency shift of 5 cm^{-1} from the laser line, in order to relate the integrated intensities and linewidths of the relaxational and collisional components to properties of the liquids.

CHAPTER II

THEORY

II.1 Background Theory

When monochromatic light is incident on a medium, a small portion of it is scattered from the beam direction. Of this portion, about 99% is Rayleigh scattered resulting in essentially no change in frequency from that of the incident beam and is due to translational and highly damped rotational motions of molecules⁽¹⁵⁾. The remaining 1% is Raman scattered and frequency shifted due to interactions with quantized rotational and vibrational energy levels of individual molecules⁽¹⁶⁾.

In liquids, the Rayleigh spectrum of scattered light consists of a Rayleigh-Brillouin triplet as well as a depolarized component known as the Rayleigh wing. The wing spectrum extends to tens of cm^{-1} for isotropic molecules⁽¹⁷⁾ and to hundreds of cm^{-1} for very anisotropic molecules such as those which can exist in liquid crystals⁽¹⁸⁾. The investigation of this "wing" is the subject of this research project.

There are a few ideas that are fundamental to the understanding of the depolarized Rayleigh wing: An incident radiation field at frequency $\nu_{\text{inc.}}$, with electric vector polarized in the "b" direction (E_b) induces a dipole moment μ_a

$$\mu_a = \epsilon_{ab} E_b / 4\pi$$

II-1

ϵ_{ab} is a tensor of rank two representing the fluctuation of the dielectric constant of the medium about an average value ϵ_0 . The magnitude of the off diagonal elements of ϵ_{ab} are a measure of the molecular anisotropy of the medium. The frequency spectrum of light reradiated by the dipole and collected at 90° to the incident radiation field is:

$$I(\nu) = C \left| \overline{\mu_a(\nu)} \right|^2 \quad \text{II-2}$$

The constant C contains the familiar ν_{inc}^4 dependence and the $1/L^2$ dependence, where L is the distance between the scattering volume and the detector. ν represents the frequency shift of the scattered radiation from the incident frequency ν_{inc} . For isolated molecules, the induced dipole moment is proportional to the difference between the polarizability parallel and perpendicular to the molecule's major axis which is defined by unit vector $\hat{r}$.

$$\mu_a \propto \Delta\alpha = \alpha_{||} - \alpha_{\perp} \quad \text{II-3}$$

The proportionality constant is a function of the azimuthal angles (θ, ϕ) of the vector $\hat{r}$.

Since there are several mechanisms which can produce a change in the polarizability (resulting in the scattering of light), a chronological survey is perhaps the simplest presentation of the developments in the depolarized Rayleigh wing field.

II.2 Developments in the Rayleigh Wing Field

The Rayleigh wing was observed as early as 1928 by Sir C. V. Raman and K. S. Krishnan⁽¹⁹⁾. They concluded that the wing spectrum was depolarized, and its intensity depended strongly on the anisotropy of the molecule.

Assuming that the local strain in a liquid is relieved by preferential rotational reorientation of molecules, M. A. Leontovich, in 1941, developed a theory which predicted a narrow depolarized line in anisotropic liquids⁽²⁰⁾. The line profile was Lorentzian, the parameter τ representing the relaxation time of the local strain.

$$I_R = \frac{I_R^0}{1 + \nu^2 \tau^2} \quad \text{II-4}$$

Leontovich's relaxational theory was later experimentally confirmed by several researchers^(21, 22). For most of the liquids studied, the Lorentzian linewidths were between 3 to 10 ghz. or .1 to .3 cm^{-1} and were therefore resolved by Fabry-Perot methods.

Leontovich's theory was adapted by Rytov, in 1957, to allow for scattering from transverse shear waves, which produce a depolarized symmetric doublet situated at about a gigahertz from the laser frequency⁽²³⁾. The narrow Lorentz and doublet are absent in molecules with spherical polarizabilities (isotropic) such as the tetrachlorides.

Since isolated atoms and spherically symmetric molecules have to the

first order isotropic polarizabilities, light scattered from them is polarized; however, on collision, the isotropic nature of the polarizability is destroyed. In 1968, Levine and Birnbaum developed a theory based on this collision-induced light scattering, which is believed to be the dominant scattering process in the far wings ($> 15 \text{ cm}^{-1}$) of noble gases⁽²⁴⁾. In their theory they considered binary collisions with straight line trajectories, and an assumed Gaussian distribution for the variation of the anisotropic polarizability with interatomic separation. The frequency spectrum is given by the expression:

$$I(\nu, T) = \int_0^\infty \int_0^\infty N(b, \nu) \left| \int_{-\infty}^\infty \mu_a(r(t)) e^{i\nu t} dt \right|^2 db d\nu \quad \text{II-5}$$

where $N(b, \nu)$ is the number of binary collisions per unit volume per unit time with relative velocity ν and impact parameter b .

$$N(b, \nu) = 2\pi n^2 (\mu/kT)^{3/2} (2/\pi)^{1/2} \nu^3 \exp\left(\frac{-\mu\nu^2}{2kT}\right) \quad \text{II-6}$$

n is the number of molecules per unit volume with reduced mass μ at a temperature T . The Fourier transform of $\mu_a(r(t))$ can be determined knowing the collision trajectory $r(t)$, which depends on the intermolecular potential. In gases, the distortion of the polarizability is predominantly due to long-ranged dipole-induced dipole (DID) effects. An incident electric field induces a dipole on an atom, which in turn induces an additional dipole on a neighbouring atom, generally not in the direction of the incident

field. This is commonly known as the Van der Waals interaction and is characterized by an attractive interaction potential:

$$U(R) \approx -1/R^6 \quad \text{II-7}$$

where R is the separation of the two dipole centers.

Combining equations II-5 and II-6, the Levine and Birnbaum model predicts, for $\nu > 10\text{cm}^{-1}$ a broad weighted exponential intensity spectrum, whose linewidth parameter ν_0 depends on the duration of the collision, and whose intensity for gases varies as the density squared.

$$I \sim I_c \sqrt{\nu} e^{-\nu/\nu_0} \quad \text{II-8}$$

The exponential weighting factor is $\sqrt{\nu}$; its importance will be demonstrated later.

In May of 1970, H. Howard-Lock, W. Gornall and B. P. Stolcheff verified that the exponential nature of the spectrum with the square root weighting factor occurred in isotropic and anisotropic liquids as well as in the gaseous state⁽²⁵⁾. They found that the linewidth parameter ν_0 could be related to the square root of the reduced mass (μ) divided by kT , with a proportionality constant γ_2^{-1} related to the distance between colliding molecules for maximum induced anisotropy.

$$1/\nu_0 = 2\pi \gamma_2^{-1} \left(\frac{\mu}{kT} \right)^{1/2} \quad \text{II-9}$$

In 1971, Bucaro and Litovitz postulated a theory appropriate to light scattering in liquids⁽²⁶⁾. At liquid densities, due to the symmetry of the close packed environment, the dipole-induced dipole mechanism is suppressed and short range electron overlap and molecular frame distortion effects predominate. They assumed a zero impact parameter for liquids, a Leonard-Jones form for the intermolecular potential

$$U(r) = \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{II-10}$$

and a $1/r^m$ form for the change in polarizability ($\Delta\alpha$) between two atoms or molecules, where "m" is a value appropriate to whether electron overlap or frame distortion processes predominate. Evaluating the fourier transform of the energy spectrum numerically, they found an intensity distribution

$$I = I_c v^{2(m-7)/7} e^{-v/v_0} \quad \text{II-11}$$

where v_0 is related to the Leonard-Jones parameters and to the factor $(\mu/kT)^{1/2}$.

For atomic liquids, the change in polarizability for an electron overlap mechanism is given by $\Delta\alpha \propto 1/r^9$, implying that $m=9$. The resulting intensity distribution

$$I = I_c v^{4/7} e^{-v/v_0} \quad \text{II-12}$$

is nearly identical to the expression found by Levine and Birnbaum

(equation II-8), although their $\sqrt{v}$ factor was a result of the mathematics of the binary collision theory. Consequently, on the basis of lineshape alone, it is not evident whether a DID (long-ranged) or an electron overlap (short-ranged) mechanism is prevalent.

For isotropic (e.g. CCl_4) and moderately anisotropic (e.g. C_6H_{12}) molecules, Bucaro and Litovitz assumed a frame distortion mechanism in which the change in polarizability depended upon the first derivative of the repulsive part of the Leonard-Jones potential, giving $m=13$ and a $12/7$ weighting term. With the $12/7$ factor, good fits were obtained for isotropic and moderately anisotropic molecules.

Also in 1971, Bucaro and Litovitz analyzed the CCl_4 Rayleigh spectrum from 2 cm^{-1} to 80 cm^{-1} (27). They found that the spectrum could be represented by a sum of two terms, one dominant at low frequencies and relaxational in character, the other dominant at frequencies greater than 15 cm^{-1} . The high frequency term is just the weighted exponential of equation II-11. The explanation of the low frequency line is not clear. Orientational scattering can be ruled out since the polarizability is a scalar, although there is a possibility of orientation due to long-lived dimers. Temperature studies by Bucaro and Litovitz from -20°C to 70°C showed that the Lorentz intensity and linewidth were constant to within 10%, apparently ruling out the possibility of dimers.

A possible explanation is given by Lewis and Van Kranendonk. Their theory, developed for rare gases, showed that radiation processes during successive binary collisions are correlated producing strong interference effects (28). Destructive interference produced a dip at zero frequency

shift in the induced infrared absorption spectrum, and constructive interference produced an additional peak in the collision-induced light scattering spectrum. The theory holds for densities such that the time between collisions is much greater than the duration of the collision. The predicted peak is ~ 65% Lorentzian in nature, and is centered at zero frequency; it has a peak intensity ~ 1/4 of the peak intensity of the collision-induced line; and has a linewidth which is inversely proportional to the time between collisions. If this theory of intercollisional interference can be applied to the liquid state, the peak is expected to occur in all liquid spectra; although for anisotropic molecules, it would be much weaker than the narrow spectrum produced by orientation fluctuations.

By the end of 1971, it was evident that although the nature of the first 10 cm^{-1} was uncertain, the higher frequency spectrum seemed to consist of a single exponential for both gases and liquids. However, J. Gersten⁽²⁹⁾ and Hyung Kyu Shin⁽³⁰⁾ experimenting on rare gases and liquids respectively, showed that graphs of $\log (I/v^{2(m-7)/7})$ versus v had several slopes which they concluded were due to the added contribution of the attractive part of the Leonard-Jones potential and therefore, the DID mechanism. Hyung Kyu Shin, using the overlap and distortion approach favoured by Bucaro and Litovitz, presented an analytical solution in the form of a weighted exponential

$$I(v) = I_c v^{(2(m-7)/7 + 4/19)} \exp(-c_1 v^{12/19} + c_2 v^{6/19}) \quad \text{II-13}$$

The pre-exponential part is similar to that of Bucaro and Litovitz¹, and also depends on the value m in $\Delta\alpha \propto 1/r^m$. However, the exponential has two terms

- a small term due to the attractive potential, dominant at low frequencies, and a larger term due to the repulsive part of the Leonard-Jones potential, dominant at high frequencies. Hyung Kyu Shin gives an expression for $1/v_0$, similar to that of Bucaro and Litovitz.

$$1/v_0 \sim \sigma (\mu/kT)^{1/2}$$

II-14

Using the distribution (II-13), he obtains reasonable fits for liquid Ar, Xe, and CCl_4 , and is able to extend the exponential region down to 3 to 10 cm^{-1} . As a result of his work, it is necessary to investigate the effect of this new distribution on the existence of the low frequency Lorentz discussed previously.

To summarize for isotropic liquids, theoretical and experimental evidence indicates that the depolarized spectrum could consist of a small relaxational component lying on a broad collisional background. The anisotropic spectra should have the above two components plus a narrow Lorentz due to orientation scattering.

The small relaxational component may be due to an intercollisional effect, while the exponential component could be due to either short-range overlap and frame distortion effects or long-range DID effects or, in fact, a combination of both; the former dominant at high frequency shifts, $>30 \text{ cm}^{-1}$, the latter dominant below 30 cm^{-1} .

It is the intention of this project to determine how the line intensities and linewidths of the various components relate to the liquid parameters.

CHAPTER III

EXPERIMENTAL APPARATUS

In order to obtain reproducible results of relative intensity measurements of the depolarized Rayleigh wing, several apparatus requirements must be satisfied.

The light source should have an hour to hour as well as a day to day stability of better than 98%. It should be intense enough to give a good signal to noise ratio ($>50:1$) but not so intense as to pose a sample heating problem. The optics should be critically aligned to completely separate the strong polarized I_V^V spectra of the tetrachlorides from their weaker depolarized I_V^H spectra. The scattering cell and liquid sample must be dust free to prevent Tyndall scattering at the laser frequency. Finally, the spectrometer should be designed to eliminate stray light, be able to scan from $+200 \text{ cm}^{-1}$ (anti-Stokes) to -200 cm^{-1} (Stokes) with varying scanning speeds, and have a wavenumber (cm^{-1}) reproducibility of $< 1 \text{ cm}^{-1}$.

The experimental apparatus will be discussed under four topics: scattering system, spectrometer, optical alignment, the scattering cell and sample preparation.

III.1 Scattering System

All the measurements in this experiment were made at 295° K and at atmospheric pressure. The scattering plane was defined as the plane through the scattering cell parallel to the direction of the incident radiation.

The scattered intensity is denoted by I_a^b , where "a" refers to the polarization of the incident field with respect to the scattering plane, and "b" refers to the polarization of the scattered field also with respect to the scattering plane. In this experiment, the polarization took on two values, "H" and "V", which refer to electric fields parallel and normal to the scattering plane respectively.

A schematic diagram of the apparatus is shown in figure I. The light source was a 17 mw. He-Ne ($6328\text{\AA}$) Stablite model 124A laser from Spectra Physics. The laser was vertically polarized to better than 1 part in 10^3 and operated in the T.E.M.₀₀ mode with a spectral width of 2 ghz. After a two hour warm-up, the laser output power was stable to within 1% over a five hour average experimental period. It has been shown that heating of the liquid sample by a 50 mw. laser beam accounts for a temperature rise of only .01° K, and is therefore expected to be negligible in this experiment⁽³¹⁾.

The laser beam was filtered by a $50\text{\AA}$ spike filter to eliminate spontaneous emission from the laser plasma. The beam was then reflected 90° by a mirror onto a half wave plate ($\lambda/2$ plate) adjusted to rotate the incident polarization (V) by 0° (V) or 90° (H) as required. A rotating polaroid positioned between the $\lambda/2$ plate and the scattering cell ensured that the incident beam was corrected for any depolarization effects occurring at the mirror or at the $\lambda/2$ plate. The diaphragm in figure I collimated the laser beam in order to avoid scattering from the cell entrance window and walls. Although it reduced the incident intensity by 20%, it reduced the scattering from an empty cell by over 50%.

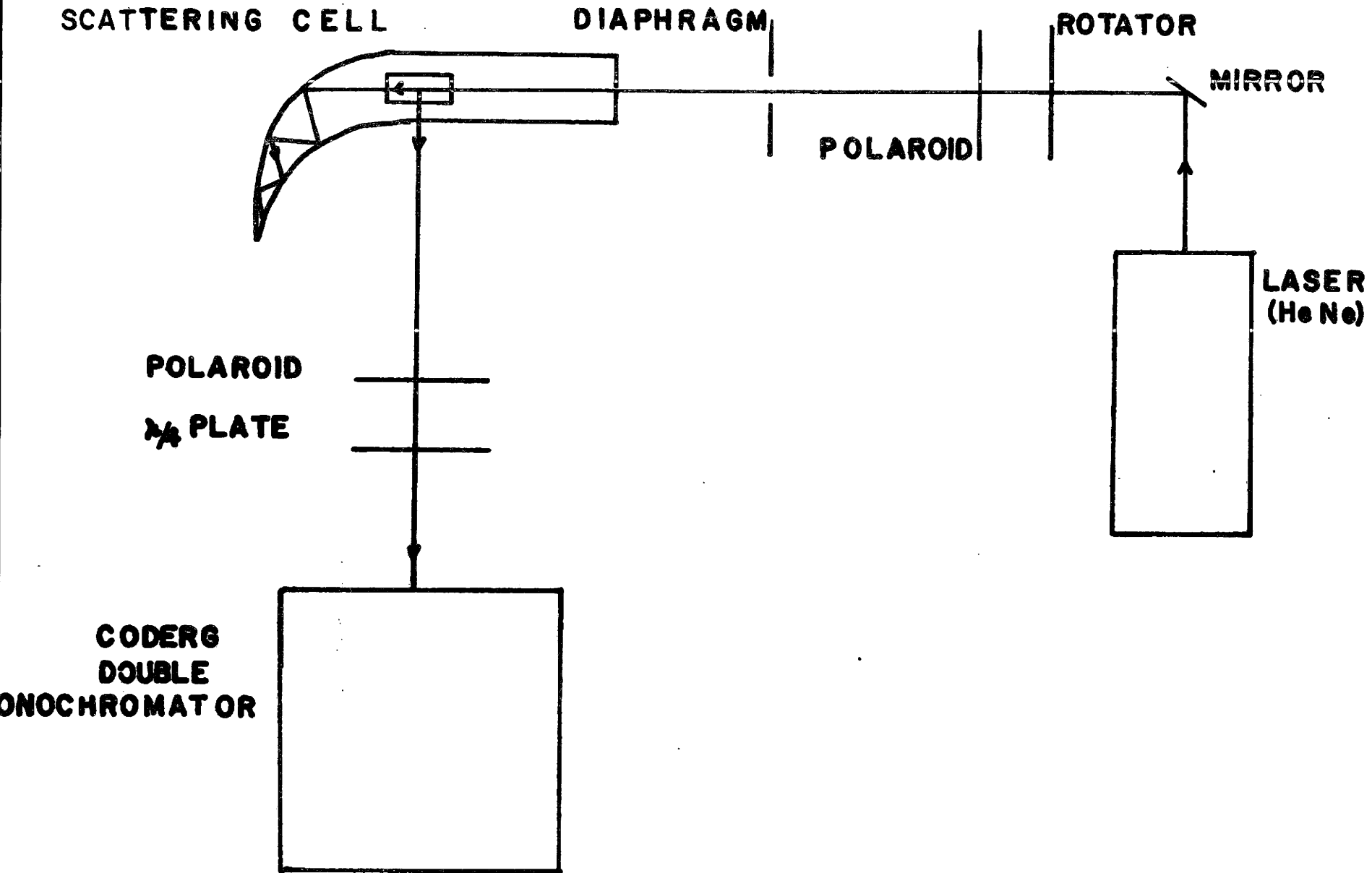


FIGURE I **SCHEMATIC DIAGRAM OF THE APPARATUS**

After passing through the diaphragm, the incident beam was focussed into the scattering cell, where it was subsequently scattered and collected by a lens at an angle of 90° to the incident beam. The scattered light was passed through another polaroid to select the scattered polarization and then frequency analyzed by a Coderg model PHO double monochromator operating with 1 cm^{-1} entrance slit widths. The detection was performed by a photomultiplier tube (EM 19558, dark current of 3×10^{-10} amperes), with the output displayed on a chart recorder.

Each spectrum was repeated three times to average out fluctuations in the laser power, drifts in the amplifier baseline, and noise due to the scattering and detection systems. For certain intense spectra, calibrated neutral density filters were used to keep the detection and amplification systems operating in their linear regions.

III.2 Spectrometer

The Coderg Raman spectrometer consisted of two monochromators in parallel. The second monochromator helped to minimize stray light entering the photomultiplier tube. Each monochromator possessed a 1200 lines/mm. diffraction grating blazed at $7500 \text{ \AA}$. The spectrometer had a scanning range of $\pm 4000 \text{ cm}^{-1}$ with a wavenumber reproducibility of $< 1 \text{ cm}^{-1}$ in the $\pm 200 \text{ cm}^{-1}$ scan range. The maximum resolution of the apparatus was about $.3 \text{ cm}^{-1}$.

Since the diffraction gratings were sensitive to the polarization of the scattered light, a quarter wave plate ($\lambda/4$ plate or scrambler) was

Inserted just after the analyzer to rotate the polarization (V or H) by 45° .

All measurements of the depolarized line were made starting from 5 cm^{-1} . This was done for several reasons. As was the case with Bucaro and Litovitz, it was very difficult in the tetrachlorides to isolate the intense Rayleigh-Brillouin triplet of the I_V^V spectrum from the weaker I_V^H spectrum⁽³²⁾. This low frequency region was also the region with the largest uncertainty due to stray light scattering. As well, three of the anisotropic molecules (C_6F_6 , $\text{C}_{14}\text{H}_{14}\text{O}_2$, $\text{C}_6\text{H}_5\text{NO}_2$) had an unresolved orientation scattering peak centered at 0 cm^{-1} with a half width determined by the spectrometer slit width. Starting from 5 cm^{-1} enabled the separation of the unresolved components from the broad background.

For all the liquids studied, the spectrometer slit width was chosen to be 1 cm^{-1} . Larger slit widths tended to broaden the strong unresolved peaks into the 5 cm^{-1} region altering both the intensity and the linewidth of the broad depolarized component. Smaller slit widths combined with the small input power into the scattering cell (6 mw.) produced a much poorer signal to noise ratio (<50:1).

A scan speed of $1 \text{ cm}^{-1}/\text{minute}$ was chosen for the unresolved lines, which had a laser plus spectrometer plus sample full width at half maximum (F.W.H.M.) of 1.5 cm^{-1} . A scan speed of $5 \text{ cm}^{-1}/\text{minute}$ was chosen for the broad spectra (F.W.H.M., $>10 \text{ cm}^{-1}$). Faster scan rates resulted in overdamping, while slower scan rates decreased the signal to noise ratio.

Since the spectrometer had a finite slit width and the laser a finite spectral width, the observed line profile $f_{\text{obs.}}(y)$ is a convolution of some apparatus function $A(x-y)$ with the true intensity distribution $\phi_{\text{t}}(x)$, which would be observed if the laser and

Instrument widths were infinitesimally narrow.

$$f_{\text{obs}}(y) = \int_{-\infty}^{\infty} \phi_{\text{t}}(x) A(x-y) dx \quad \text{III-1}$$

Knowing the spectral lineshape and linewidth of the laser plus spectrometer (Gaussian for T.E.M.₀₀ mode, F.W.H.M. of 1.4 cm^{-1}), and that of the observed line (predominantly dispersion in form, F.W.H.M. $> 10 \text{ cm}^{-1}$), the true distribution intensity and F.W.H.M. could be found graphically⁽³³⁾. The corrections to the intensity and F.W.H.M. were less than 4% for most of the broad depolarized spectra. This was confirmed experimentally by varying the slit width or apparatus function width and noting the change in the half width at half intensity of the depolarized spectra taken from 5 cm^{-1} . No significant change was noted up to slit widths of 2 cm^{-1} .

III.3 Optical Alignment

The procedure for aligning the polarizer, $\lambda/2$ and $\lambda/4$ plates was as follows:

The power from the vertically polarized He-Ne laser was measured using an Optics Technology model 610 powermeter calibrated in milliwatts. The vertical axis of easy transmission of the polaroid was determined by inserting it between the laser and the detector and rotating it for a maximum signal. The difference in the power readings due to the polaroid absorption was about 25%. The horizontal axis could be found by rotating the polaroid for a minimum signal. Crossed polaroids gave an extinction ratio of 4×10^{-4} .

Next a $\lambda/2$ plate was inserted between the vertically aligned polaroid and the laser and was rotated to give a maximum signal (absorption of $\lambda/2$ plate $\sim 10\%$). This corresponds to a null (0°) rotation of the laser polarization (V). The $\lambda/2$ plate was then rotated to extinguish the signal (i.e. crossed polaroid condition) and therefore corresponded to a 90° rotation of the laser polarization. Using this alignment method, the transmitted powers from the $\lambda/2$ plate in the "V" and "H" positions were within 2% of each other.

The $\lambda/4$ plate was substituted for the $\lambda/2$ plate between the laser and the vertically aligned polarizer and was aligned as follows: Knowing the absorption losses of the polarizer ($\sim 25\%$) and the $\lambda/4$ plate ($\sim 10\%$), the power transmitted by the $\lambda/4$ plate and polarizer at perfect alignment could be calculated. The $\lambda/4$ plate was rotated until this power reading was obtained. The polarizer was then rotated by 90° (i.e. from, V to H) and small adjustments of the $\lambda/4$ plate were made to obtain the same power reading as with the polarizer vertical.

III.4 Scattering Cell and Sample Preparation

The scattering cell was designed to minimize stray light scattering. It consisted of a 1/2" diameter, thin walled glass cylinder drawn into a trapping Woods horn configuration. The cell was painted with flat, black paint except for an entrance and exit slit. It was positioned in a standard rectangular Raman cell holder with its cylindrical axis parallel to the scattering plane. The unscattered laser beam would hit the back of the horn

and be multiply reflected down the horn and trapped.

Great care was taken to remove dust from the liquid samples and the scattering cell, since a small amount of dust could produce enough scattering near 0 cm^{-1} to obliterate the liquid spectra in this region. Before each run, the scattering cell was flushed out twice with methanol followed by carbon tetrachloride. The liquid samples were filtered using a mill-micropore filter driven by extremely pure N_2 gas. After this procedure, passage of the focussed laser beam through the cell produced no visual Tyndall scattering. For liquids SiCl_4 , GeCl_4 , TiCl_4 , which react violently with the water vapour in the atmosphere, vacuum distillation methods were used to obtain clean samples.

For weak depolarized scatterers such as the tetrachlorides, the stray light entering the I_V^H spectrum at zero frequency was less than 10%. This percentage was reduced to 1% for the I_V^H , I_V^V spectra of the anisotropic molecules and the I_V^V spectra of the isotropic molecules. In all liquids, the contribution of stray light at 5 cm^{-1} was negligible.

CHAPTER IV

OBSERVED SPECTRA

The liquids studied in this experiment are listed in Table I along with selected characteristic parameters: column 1 lists the molecular weights (mol. wt.); column 2, the density (ρ); column 3, the ionization potential (I.P.); column 4, the index of refraction (n); column 5 the dipole moment; and column 6, the viscosity (η).

The liquids were chosen so that their intensities and linewidths could be studied over a wide set of molecular configurations. The isotropic molecules are represented by four tetrachlorides, XCl_4 , where the X atom occupies the center and the Cl atoms the corners of a tetrahedron. The moderately anisotropic molecules are represented, in order of increasing anisotropy, by C_6H_{12} , C_6H_6 , C_6F_6 . C_6H_{12} consists of a benzene ring with each carbon having two hydrogen atoms in an out of plane bridge structure. C_6F_6 is a simple benzene ring structure with fluorine atoms replacing the hydrogen atoms. Finally, the very anisotropic molecules are represented by benzyl benzoate (two benzene rings joined by a $\begin{smallmatrix} \text{O} & \text{H} \\ \parallel & | \\ -\text{C} & -\text{O} & -\text{C} & -\text{H} \end{smallmatrix}$ bridge) and nitrobenzene (benzene ring with NO_2 radical substituted for a benzene hydrogen atom).

IV.1 Total Integrated Intensities

Table II summarizes the observed polarized I_V^V and depolarized I_V^H integrated intensities normalized to the 459 cm^{-1} line in CCl_4 , which is

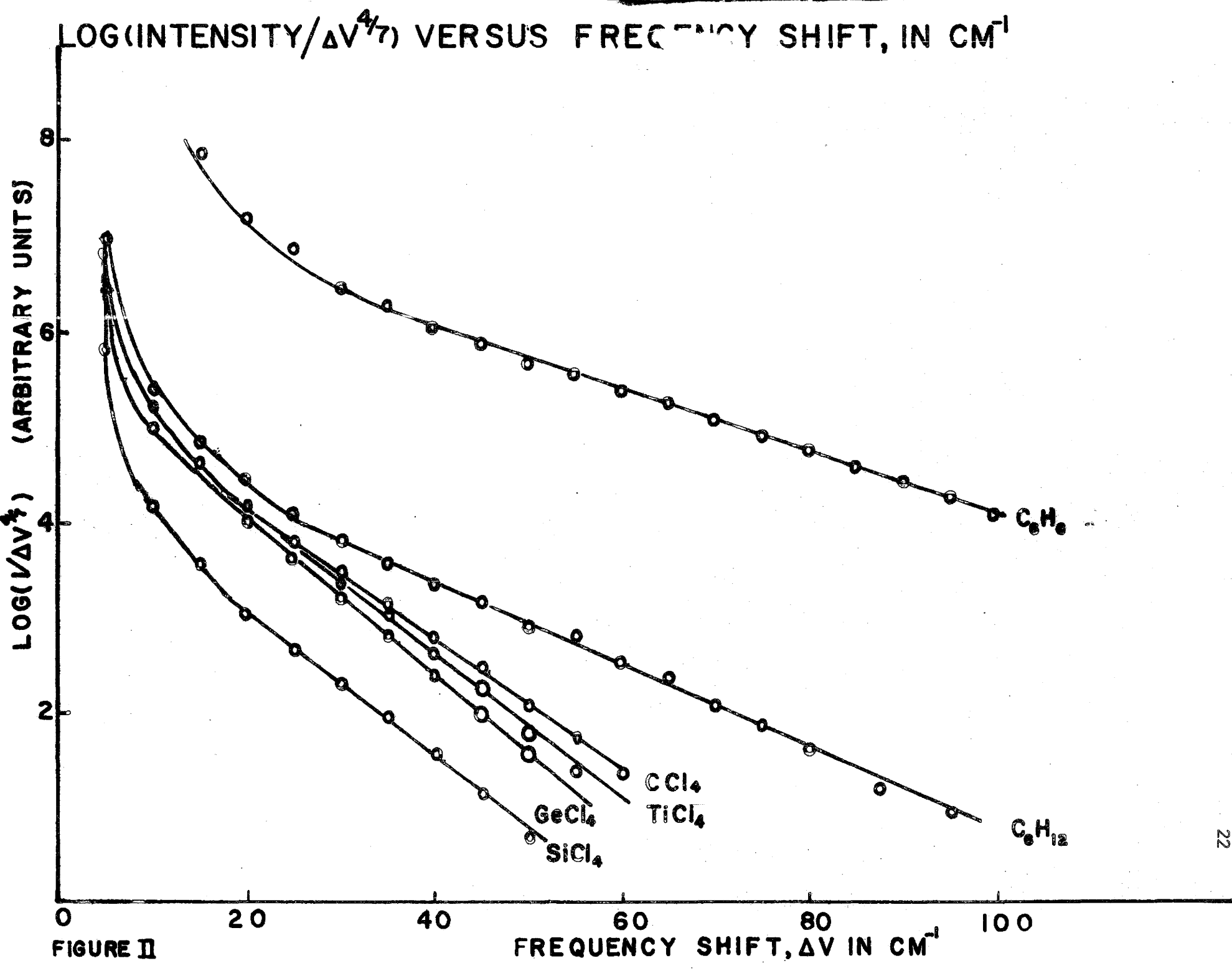
frequently used as an intensity standard in Raman Spectroscopy. In both columns 1 and 2, the integrated intensities were determined starting from 0 cm^{-1} (a), while for column 3, they were determined starting from 5 cm^{-1} (b).

The errors on the integrated intensities are roughly 15%: 5% is representative of the standard error found by repeating each run three times, 10% is an estimate of the day to day experimental reliability. The 10% includes errors due to the day to day variation of the sample cell alignment and laser fluctuations. Since all intensity ratios in this report were taken from one set of results, their error is about 10%.

All liquids possessed an intense I_V^V (a) spectrum (table II, column 1); however, the depolarized intensity I_V^H (a) (table II, column 2) increased by a factor of 100 with the progression to increased anisotropy. Since there is very little integrated intensity data available in the literature, the only comparison to the results of table II is the I_V^H (a) intensity ratio for $\text{C}_6\text{H}_5\text{NO}_2/\text{C}_6\text{H}_6$ which is given by reference (36) as 4.7 and by reference (37) as 7.2. The value for this experiment of $6.2 \pm .6$ falls in reasonable agreement between the two quoted values.

IV.2 Intensity Lineshape.

Plots of $\log (I/v^{4/7})$ versus v (figure II) indicate that the tetrachlorides as well as C_6H_{12} are fit very well above 15 to 20 cm^{-1} by an exponential intensity distribution with a $r=4/7$ in the v^r weighting term of equation II-1. For the anisotropic molecules, the range of linear



fit could be extended from 125 to 150 cm^{-1} using the $r = 12/7$ power in ν^r . In both cases, there was only a single linear region, contrary to that observed by J. Gersten and Hyung Kyu Shin, indicating that short-range effects alone can account for the observed lineshape. Use of Hyung Kyu Shin's distribution (equation II-13) did extend the range of linear fit at low frequencies by 5 to 10 cm^{-1} but only at the expense of 5 to 10 cm^{-1} in the high frequency region. The distribution could not account for the sharp rise in intensity in the tetrachlorides at $\nu < 10 \text{ cm}^{-1}$ and therefore did not rule out the possibility of a Lorentz at low frequencies due to the intercollisional effects.

IV.3 Depolarization Ratios

Column 4 of table II lists the depolarization ratios ρ_v defined as $\rho_v(a) = I_v^H(a)/I_v^V(a)$. The subscript "v" in ρ_v indicates that the incident light is vertically polarized. ρ_v can be related to the depolarization ratio for unpolarized light ρ_u by ⁽³⁸⁾

$$\rho_u = 2\rho_v/(1 + \rho_v) \quad \text{IV-1}$$

From elementary theoretical considerations, both ρ_u and ρ_v should be zero for the Rayleigh and Brillouin components scattered at 90° ⁽³⁹⁾. Experimentally, there is a departure from zero in the order of 1 or 2% for most liquids ⁽⁴⁰⁾. The non-zero ρ_v for the Rayleigh Brillouin triplet combined with the broad depolarized background account for the non-zero $\rho_v(a)$ observed in column 4 of table II. In the anisotropic molecules, there is an additional depolarizing

effect due to the orientational scattering predicted by Leontovich. It is predominantly the contribution of this strong depolarized component which accounts for the increase in $\rho_v(a)$ (column 4, table II) with an increase in molecular anisotropy.

Column 5 of table II, $\rho_v^{ref}(a)$, lists values of ρ_v from the literature. Considering the great uncertainties near 0 cm^{-1} , the agreement, in most cases, is very good.

In a frequency region where the intensity contribution of the polarized triplet is negligible compared to the depolarized background, the theoretical value of ρ_v approaches .75⁽⁴⁵⁾. Depolarization measurements of $\rho_v(b) = I_V^H(b)/I_V^V(b)$ were made on all liquids starting from 5 cm^{-1} . $\rho_v(b)$ for the tetrachlorides was consistently low ($.55 \pm .03$), while for the anisotropic molecules, the $\rho_v(b)$ of $.72 \pm .01$ did approach the theoretical limit. Values of $\rho_v(b)$ for the tetrachlorides at selected frequencies from 5 cm^{-1} to 80 cm^{-1} were also low. A possible explanation is that since the average ratio of I_V^V/I_V^H at $\nu = 0 \text{ cm}^{-1}$ in the tetrachlorides is 1000:1, the strong polarized triplet $I_V^V(a)$ (F.W.H.M. 1.5 cm^{-1}) could enter the $I_V^V(b)$ region as a broad tail, consequently increasing $I_V^V(b)$ and reducing $\rho_v(b)$. Experimental evidence seems to agree with this explanation. The half widths of the tetrachloride $I_V^V(b)$ spectra were narrower than those of the $I_V^H(b)$ spectra, contrary to those observed with the anisotropic molecules where the two half widths were nearly equal. With a reduction in the spectrometer slit width from 1 cm^{-1} to $.5 \text{ cm}^{-1}$, the triplet F.W.H.M. was narrowed, while the H.W.H.M. of the $I_V^V(b)$ spectra increased to approach

the H.W.H.M. of the $I_V^H(b)$ spectra. The depolarization ratio increased on an average from .55 to .65. Unfortunately, due to a weak signal to noise ratio, the slit width could not be reduced less than $.5 \text{ cm}^{-1}$ to see if the ratio further approached .75.

List of the liquids studied and selected parameters. Unless otherwise stated, values were taken from the Handbook of Chemistry and Physics, 50th. edition.

	Formula	Mol. Wt.	$\rho_{20^{\circ}\text{C}}$ g/cc	I.P. e.v.	n	Dipole* Moment (Debye)	$n_{20^{\circ}\text{C}}$ cp
Silicon Tetrachloride	SiCl_4	169.9	1.48	11.79 ⁽³⁴⁾	1.41	0.	--
Germanium Tetrachloride	GeCl_4	214.4	1.84	11.88 ⁽³⁴⁾	1.46	0.	--
Titanium Tetrachloride	TiCl_4	189.7	1.73	--	1.61	0.	--
Carbon Tetrachloride	CCl_4	153.8	1.59	11.47 ⁽³⁴⁾	1.47	0.	1.0
Cyclohexane	C_6H_{12}	84.2	.78	9.8	1.42	0.	1.0
Benzene	C_6H_6	78.1	.88	9.2	1.50	0.	.7
Hexafluorobenzene	C_6F_6	186.1	1.62	10.	1.38 ⁽³⁵⁾	0.	.9
Benzyl benzoate	$\text{C}_{14}\text{H}_{14}\text{O}_2$	214.1	1.16	--	1.57	2.	8.3
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$	123.1	1.20	9.9	1.55 ^{**}	4.	2.0

* A. L. McLellan, Tables of Experimental Dipole Moments (W.H. Freeman Co., San Francisco, 1963)

** International Critical Tables of Numerical Data, Physics, Chemistry and Technology, (McGraw Hill Publishing Company, New York, 1928).

TABLE II

Polarized and depolarized intensities relative to the 459 cm^{-1} line of CCl_4

	I_V^V (a)	I_V^H (a)	I_V^H (b)	ρ_V (a)	ρ_V (a) ^{ref.}
SiCl_4	280.*	1.7*	.42	.006	--
GeCl_4	100.	1.2	.77	.013	--
CCl_4	90.	1.2	.80	.013	.019 ⁽⁴¹⁾
TiCl_4	150.*	2.1*	.83	.014	--
C_6H_{12}	75.	1.4	1.0	.02	.02 ⁽⁴²⁾
C_6H_6	170.	26.	15.	.15	.27 ⁽⁴²⁾
C_6F_6	130.	50.	8.	.36	.3 ⁽⁴³⁾
$\text{C}_{14}\text{H}_{14}\text{O}_2$	140.	70.	9.	.52	--
$\text{C}_6\text{H}_5\text{NO}_2$	320.	160.	18.	.52	.52 ⁽⁴⁴⁾

(a) Stokes side from $0.\text{ cm}^{-1}$

(b) Stokes side from $5.\text{ cm}^{-1}$

* To be taken as maximum due to Tyndall scattering.

CHAPTER V

DATA ANALYSIS

V.1 Curvefitting Procedure

As mentioned in Chapter II, theoretical and experimental considerations indicate that the depolarized spectra of the isotropic liquids can adequately be described by a narrow relaxational component resting on a broad, collisional background. Since the orientation components of C_6F_6 , $C_{14}H_{14}O_2$, $C_6H_5NO_2$ are confined to $< 5 \text{ cm}^{-1}$, these liquids should also be described by a relaxational and a collisional component. C_6H_6 and C_6H_{12} are more complicated since their orientation component extends well into the 5 cm^{-1} region. For consistency, the intensity profiles of all the liquids were curvefit from 5 cm^{-1} using the following functional form:

$$I_{Th} = \frac{I_R^5}{1 + \left(\frac{\nu-5}{\sigma_R^5}\right)^2} + I_C^5 \nu^r e^{-\nu/\nu_0} \quad V-1$$

Since the actual Lorentz should be centered at 0 cm^{-1} , the first term is an approximation of the Lorentz line profile starting at 5 cm^{-1} . This approximation should not greatly effect relative intensity ratios and linewidths. The parameters I_R^5 , σ_R^5 represent the peak intensity and half width at half maximum of the Lorentz from 5 cm^{-1} respectively. The second term represents the broad collisional component. I_C^5 is the intensity of the collisional component at 5 cm^{-1} , while ν_0 is the collisional linewidth parameter. The quantity "r" in the exponential weighting term

v^r is either 4/7 or 12/7 depending on whether Bucaro and Litovitz' electron overlap or frame distortion mechanism predominates.

The collision distribution has a maximum at $v = rv_0$

$$I_c^{\max.} = I_c^s (rv_0)^r e^{-r} \quad V-2$$

The position and magnitude of this maximum vary with the power "r" and parameter v_0 , resulting in different intensity contributions for the 4/7 and 12/7 powers. Since the exponential distribution is an asymptotic expression valid for $v > rv_0$, the region $v < rv_0$ (usually about 5 to 20 cm^{-1}) was approximated by a straight line nearly tangential to the peak maximum. The approximation gives a similar collision lineshape as Bucaro and Litovitz' numerically evaluated distribution, which was valid down to zero frequency shifts⁽⁴⁶⁾.

The lineshape parameters were obtained as follows: The linear nature of the plots of $\log(I/v^r)$ versus v (figure II) indicate that for $v > 20 \text{ cm}^{-1}$, the intensity distribution is predominately exponential. The slope of each line gives an accurate estimate of v_0 . Knowing v_0 , "r", and several values of the total intensity in the linear frequency region, average values of I_c^s and $I_c^{\max.}$ can be calculated using equations V-1 and V-2 respectively. The value of I_R^s can be found by simply subtracting $I_c^{\max.}$ from the total observed intensity at 5 cm^{-1} . The slope of a $(I_R^s/I - 1)$ versus $(v - s)^2$ graph for $v < 15 \text{ cm}^{-1}$ gives an estimate of $(\sigma_R^s)^2$.

When the parameters ν_0 , I_V^S , σ_R^S were varied simultaneously, ν_0 increased and I_C^S decreased substantially from their experimental values. To avoid this, two parameters σ_R^S and I_C^S were used in the curve-fitting at a fixed value of ν_0 . A coarse grid was performed on ν_0 with each value having the same initial parameters σ_R^S , I_C^S . The procedure was repeated with finer grids on ν_0 until the best fit was achieved.

The curvefitting was done using least square fitting techniques with a Chi square (χ^2) goodness of fit test defined as

$$\chi^2 = \sum_i \left(\frac{I_{\text{exp.}}(\nu_i) - I_{\text{Th.}}(\nu_i)}{\sigma(\nu_i)} \right)^2 \quad \text{V-3}$$

$I_{\text{Exp.}}(\nu_i)$, $I_{\text{Th.}}(\nu_i)$ are the experimental and theoretical intensities at frequency ν_i with standard error $\sigma(\nu_i)$. The standard error was found by repeating each spectrum three times and obtaining the average deviation from the mean intensity at 2.5 cm^{-1} intervals. It amounted to 3 to 5% for most liquids. The criterion for a good fit was the Chi square per degree of freedom (χ^2/N) test. N is the number of degrees of freedom and equals the number of data points fitted minus the number of parameters varied in the fit (47). Values of the parameters were generated by the curvefitting program until χ^2/N approached unity and the parameters converged to physically acceptable values. χ^2 for a parameter A and its increments $A \pm \Delta A$ were least squares fitted to a parabola, and the change in the parameter corresponding to a minimum χ^2 with a change in χ^2 of unity represented an estimate

of the standard error of the varied parameter⁽⁴⁸⁾.

In order to compare the fits of $r = 4/7$ to $r = 12/7$, only the frequency region $\nu > 12/7 \nu_0$ (value of ν_0 found using 12/7 power) was considered. This eliminated uncertainties of the linear approximation and the presence of the Lorentz.

V.2 Curvefitting Results

Figure III shows the relaxational and collisional components of a representative tetrachloride (CCl_4). Figure IV shows similar components for nitrobenzene which is representative of the very anisotropic molecules. In both cases, excellent fits were obtained for both low ($\nu < 15 \text{ cm}^{-1}$) and high frequency ($\nu > 60 \text{ cm}^{-1}$) regions. The anisotropic molecules show a strong increase in the ratio of the peak relaxational to collisional intensity at 5 cm^{-1} . The relaxational component makes the predominant contribution to the intensity in the first 25 cm^{-1} but becomes negligible relative to the collisional component by 60 cm^{-1} .

Table III displays the final curvefitting parameters σ_R^S and ν_0 (c. fit) along with their correlation times defined by $\tau_R(\text{sec}) = \frac{1}{2\pi c \sigma_R^S (\text{cm}^{-1})}$, $\tau_C(\text{sec}) = \frac{1}{2\pi c \nu_0 (\text{cm}^{-1})}$, where c is the speed of light.

Column 1 of table IV lists the experimental values of ν_0 (exp) taken from the plots of $\log(I/\nu^r)$ versus ν for $r = 4/7$ and $12/7$. Column 2 shows the corresponding curvefit values ν_0 (c. fit). In every case, subtraction of the Lorentz from the total intensity changed ν_0 (c. fit)

RELAXATIONAL AND COLLISIONAL COMPONENTS OF CARBON TETRACHLORIDE

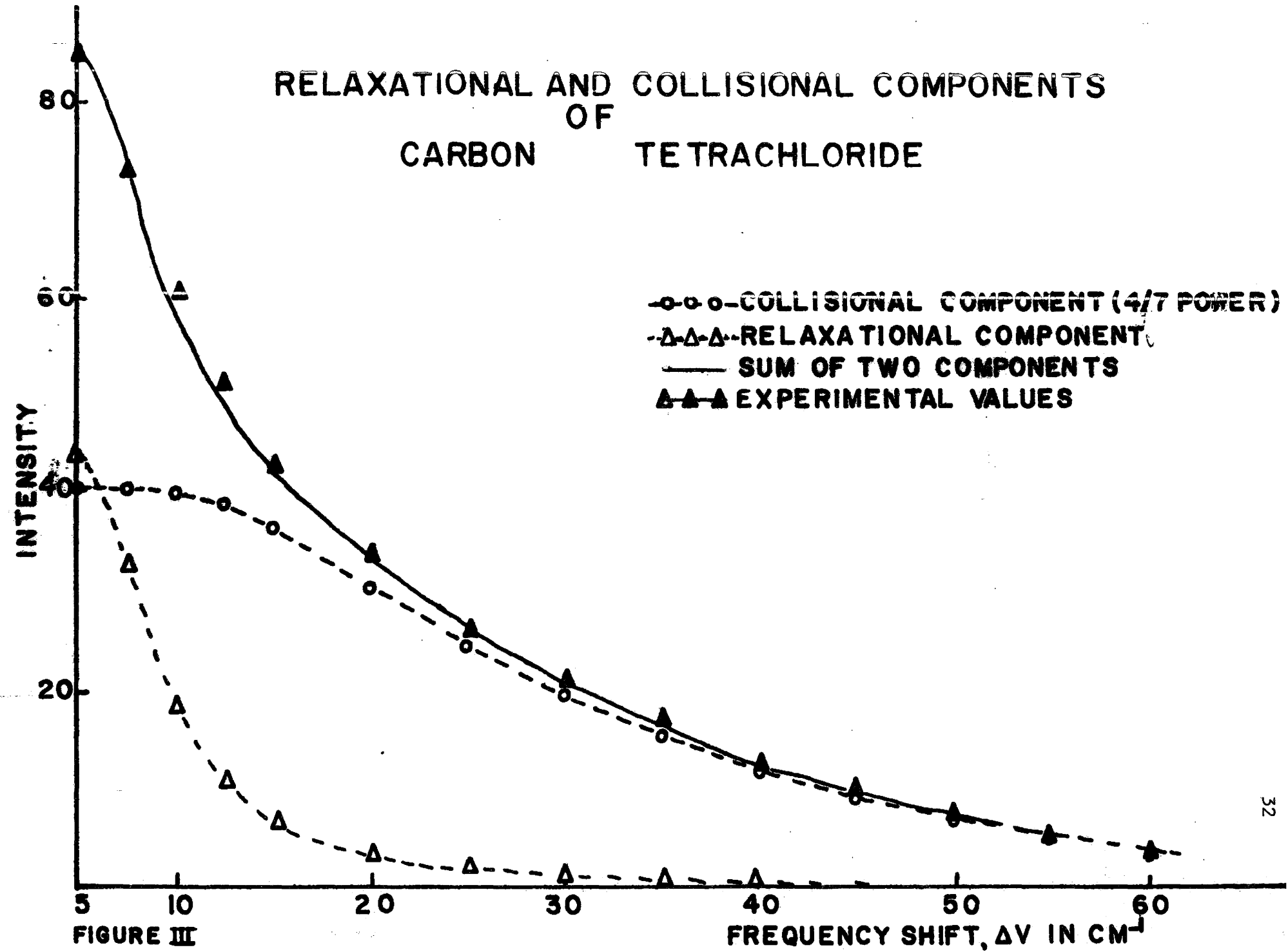


FIGURE III

RELAXATIONAL AND COLLISIONAL COMPONENTS OF NITROBENZENE

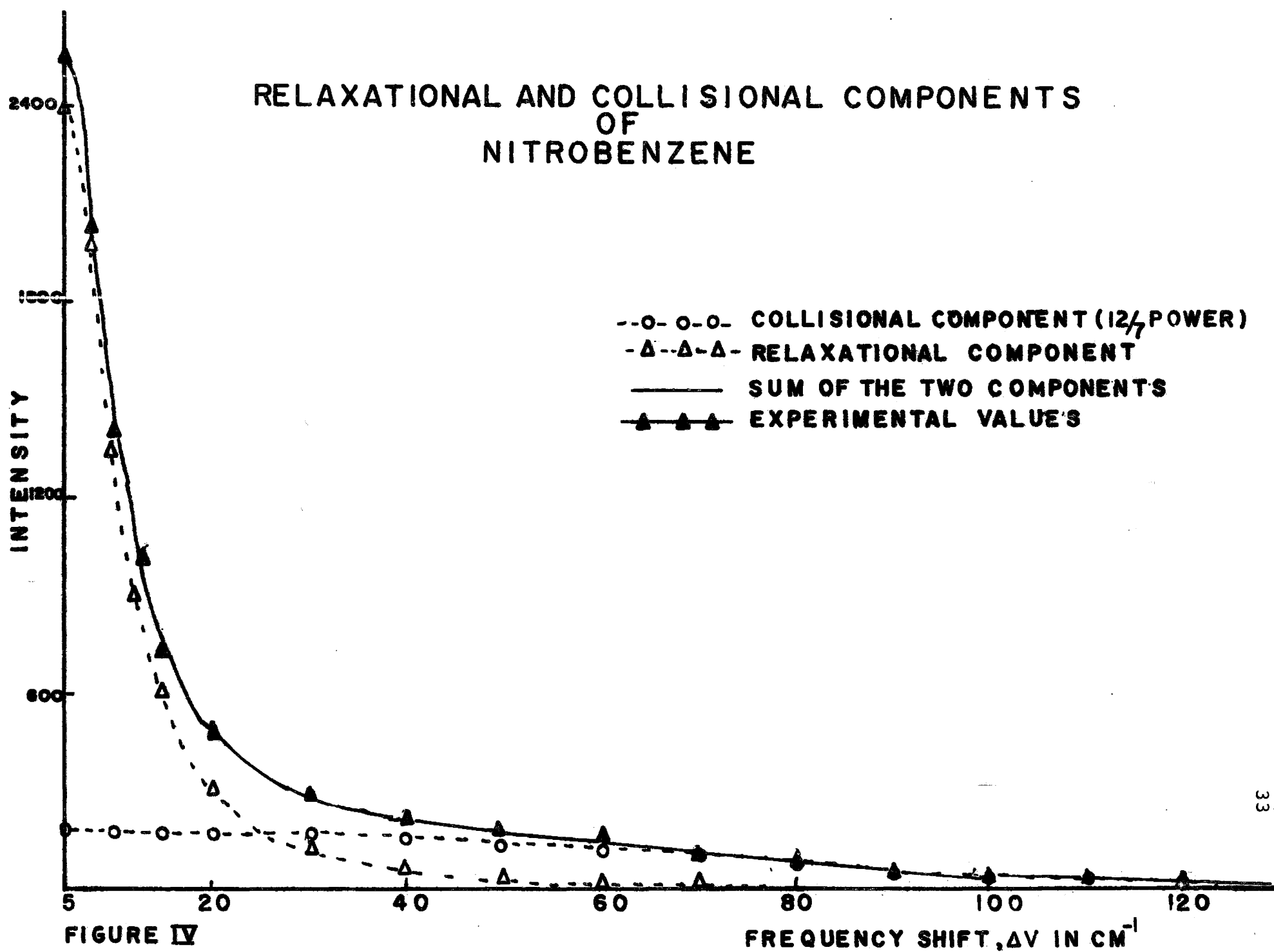


FIGURE IV

FREQUENCY SHIFT, $\Delta\nu$ IN cm^{-1}

from ν_0 (exp) by less than 10%. Column 3 gives curvefit values ν_0 (c.fit) found using data obtained on a Spex Spectrometer with $.5 \text{ cm}^{-1}$ slits and a 40 mw. He-Ne laser. The two sets of values for ν_0 (c. fit) agree exceedingly well, indicating the consistency of the results under widely varying experimental conditions. Column 4 gives the χ^2/N for the 4/7 and 12/7 powers calculated starting from $\nu = r\nu_0$. The χ^2/N values are also very representative of the goodness of fit over the entire frequency range. the χ^2/N results indicate a trend toward better fits using the 4/7 power for isotropic molecules and the 12/7 power for anisotropic molecules. Unfortunately, the trend is not strong enough to definitely select the electron overlap and frame distortion mechanisms as the primary scattering mechanisms for isotropic and anisotropic molecules respectively.

The integrated intensities of each component were obtained as follows: The integrated intensity of the Lorentz $I_V^H(R)$ from 5 cm^{-1} to infinity is just proportional to the product of I_R^S and σ_R^S (Appendix I) and can therefore readily be calculated. Since the fits were excellent, the collisional integrated intensity $I_V^H(C)$ was found by simply subtracting the relaxational intensity $I_V^H(R)$ from the total experimental intensity $I_V^H(T)$. The results of $I_V^H(T)$, $I_V^H(R)$, $I_V^H(C)$ and the peak intensity ratios of $I_V^H(R)/I_V^H(C)$ at 5 cm^{-1} are recorded in Columns 1 to 4 respectively, in table V.

As mentioned previously, the intensities of the collisional and relaxational distributions are different for the 4/7 and the 12/7 powers. In all cases, the collisional intensity for the 12/7 power is about 15% lower than that obtained with the 4/7 power.

V.3 Relative Intensity Ratios of the Relaxational Component

Discussion of the integrated intensities of the relaxational component will occur in two sections dealing with isotropic and anisotropic molecules respectively.

As mentioned in Chapter II, Lewis and Van Kranendonk predict, for rare gases, a peak predominately Lorentzian in nature centered at zero frequency and with a peak intensity $1/4$ that of the collisional component. If this intercollisional effect is responsible for the observed relaxational component in the tetrachlorides, the peak intensities, as well as the integrated intensities relative to the collisional component, are enhanced in the liquid state. With the present uncertainties, the relaxational component in the tetrachlorides will hereafter be referred to as the isotropic relaxational component and not as the intercollisional component.

From $\log I(R)$ versus $\log \rho$ plots, the relaxational intensities seem to be a strong function of the liquid densities (ρ^L), but since there are several other parameters which may vary from molecule to molecule, such as the reduced mass, it is hard to ascertain the exact density dependence. Density studies on the relaxational component, now being performed by T. A. Litovitz et al, will certainly clarify the situation. It is still assumed that this component enters into the scattering distribution of all liquids.

Without knowledge of the dependence of the isotropic relaxational component on the molecular parameters, it is very difficult to estimate the size of this component in the anisotropic molecules (C_6F_6 , $C_{14}H_{14}O_2$, $C_6H_5NO_2$). If the strong density dependence is correct, the isotropic relaxational contribution to the observed anisotropic relaxational component would be quite small ($<15\%$). It's therefore possible that some other

scattering process accounts for the strong relaxational component in the anisotropic molecules at 5 cm^{-1} . Orientation scattering is ruled out since in these molecules it produces an unresolved peak centered at zero frequency and has been found experimentally to contribute to less than 10% of the intensity at 5 cm^{-1} . However, a second major component has in fact been observed by Zaitsev and Starunov⁽⁴⁹⁾ in 1965, and by Craddock et al., in 1968⁽⁵⁰⁾. The spectrum of depolarized light scattered in various anisotropic liquids consisted of more than one Lorentz and could be successfully described by a sharp Lorentz on a broader Lorentzian pedestal.

In 1969, A. V. Sechkarev and P. T. Nikolaenko developed a theory which predicted a narrow Lorentz on a similar broad background⁽⁵²⁾. They assumed that during the average time τ between Brownian reorientations, each molecule of the liquid executes quasielastic rotational oscillations in a potential well with an average angular frequency ω_{osc} . (Period $\tau_{\text{osc}} = \pi/\omega_{\text{osc}} = 10^{-12}$ sec.). The oscillations are perturbed by irregular impact interactions of frequency Z . τ was previously interpreted by Leontovich as the relaxation time of fluctuations in the anisotropy; for C_6F_6 , $\text{C}_{14}\text{H}_{14}\text{O}_2$, $\text{C}_6\text{H}_5\text{NO}_2$ $\tau \sim 10^{-10} - 10^{-11}$ seconds⁽⁵²⁾.

The rotational-oscillation theory predicts a narrow Lorentz identical to that found by Leontovich

$$I_b = I_b^0 / (1 + \tau^2 \omega^2)$$

V-4

(see Chapter II, equation II-4) and also a broad Lorentz squared intensity distribution in the wing, approximated by

$$I_w \sim \frac{I_w^0}{(1 + w^2/Z^2)^2} \quad \text{V-5}$$

provided that $Z/w_{\text{osc.}} > 1$, $\tau_{\text{osc.}}/\tau < 10^{-1}$. The interesting point to note is that the half width at half maximum (H.W.H.M.) of this distribution is a measure of the time between collisions. This is the same H.W.H.M. dependence as found in Lewis and Van Kranendonk's intercollisional theory. Therefore, although the contribution of the isotropic and rotational-oscillation processes to the observed anisotropic relaxational component are uncertain, in both cases the half width parameters depend on the time between collision. The importance of this dependence will be demonstrated in V.4.

The last section deals with the particular cases of C_6H_6 and C_6H_{12} which also contain an orientation peak in the 5 cm^{-1} region. To isolate each component, the intensity contribution in the far wings, which is predominately due to short-ranged collision induced scattering can be found and subtracted from the total intensity. The remaining spectrum can be curvefit using Lorentz and Lorentz squared distributions corrected for the contribution of the isotropic relaxational component. Due to the uncertainty in the isotropic relaxational component and to the complexity of this problem, the decomposition procedure was not carried out.

V.4 Relaxational Linewidth

As demonstrated in the last section, the relaxation time of the isotropic and anisotropic relaxation component could theoretically be identified with the time between collisions τ_R . Experimentally, this time varies from molecule to molecule by only 15%, which is surprising considering the wide range of molecular masses, densities, and anisotropies involved. The following is a possible simple explanation: Assuming that between collisions two molecules travel toward each other with an average relative velocity $\bar{v}$, through a mean free path $\bar{l}$, then the time between collisions, τ_R , will be given by

$$\tau_R = \bar{l} / \bar{v}$$

In a gaseous approximation $1/2 \mu \bar{v}^2 = kT$ or $\bar{v} = \sqrt{T/\mu}$. The distance $\bar{l}$ will depend inversely on the product of the number of molecules per unit volume times the mean collisional cross-section area per molecule. As will be demonstrated in the section entitled "Collision Linewidth", this cross-section is almost constant for the molecules studied. The number of molecules per unit volume equals $\frac{\rho}{2\mu}$, giving τ_R proportional to $\mu^{3/2}/\rho T^{1/2}$. For liquids at the same temperature, τ_R varies as $\mu^{3/2}/\rho$. For each molecular liquid, this simple model predicts that the time between collisions varies inversely as the density of the liquid. This is consistent with the relation found by Lewis and Van Kranendonk in Chapter II.

Using the $\mu^{3/2}/\rho$ relation, calculation of the possible τ_R ratios

for all possible pairs of liquids studied (excluding ratios involving C_6H_6 , C_6H_{12} , $C_{14}H_{14}O_2$ gave an average value of $1.2 \pm .2$. The experimental ratios were found using τ_R corresponding to the 4/7 power for isotropic molecules and τ_R corresponding to the 12/7 power for the anisotropic molecules. The experimental value was $1 \pm .1$, in very good agreement with the simple gaseous model. An interesting consequence of these ratios is that they predict that the time between collisions is very similar in all the liquids studied regardless of their widely varying molecular parameters.

The ratios involving benzyl benzoate, which consists of two connected benzene rings, agreed with the model predictions if $\mu/2$ instead of μ was used in the $\mu^{3/2}/\rho$ relation. Experimental ratios of τ_R involving C_6H_6 and C_6H_{12} were different from the model predictions by several standard errors, consistent with their relaxational component being comprised of an additional peak due to orientation scattering.

All the experimental values for σ_R^5 , τ_R presented in table III have been determined from a Lorentz centered at 5 cm^{-1} . As mentioned this was done to avoid uncertainties for $\nu < 5 \text{ cm}^{-1}$ due to stray light scattering, non-zero Rayleigh-Brillouin triplet depolarization ratios, unresolved orientation components, and sample cell alignment errors. The values of σ_R^0 , τ_R^0 of a Lorentz centered at 0 cm^{-1} can be obtained in the following way: Graphs of Lorentz distributions with a range of H.W.H.M. parameters σ_R^0 were plotted and interpolated at 5 cm^{-1} to find the corresponding value of σ_R^5 . A plot of σ_R^0 versus σ_R^5 gives a straight line (valid for σ_R^5 in the 4 to 7 cm^{-1} region) with slope of nearly $\sqrt{2}$ and zero intercept. Therefore

σ_R^O can be found from the relation

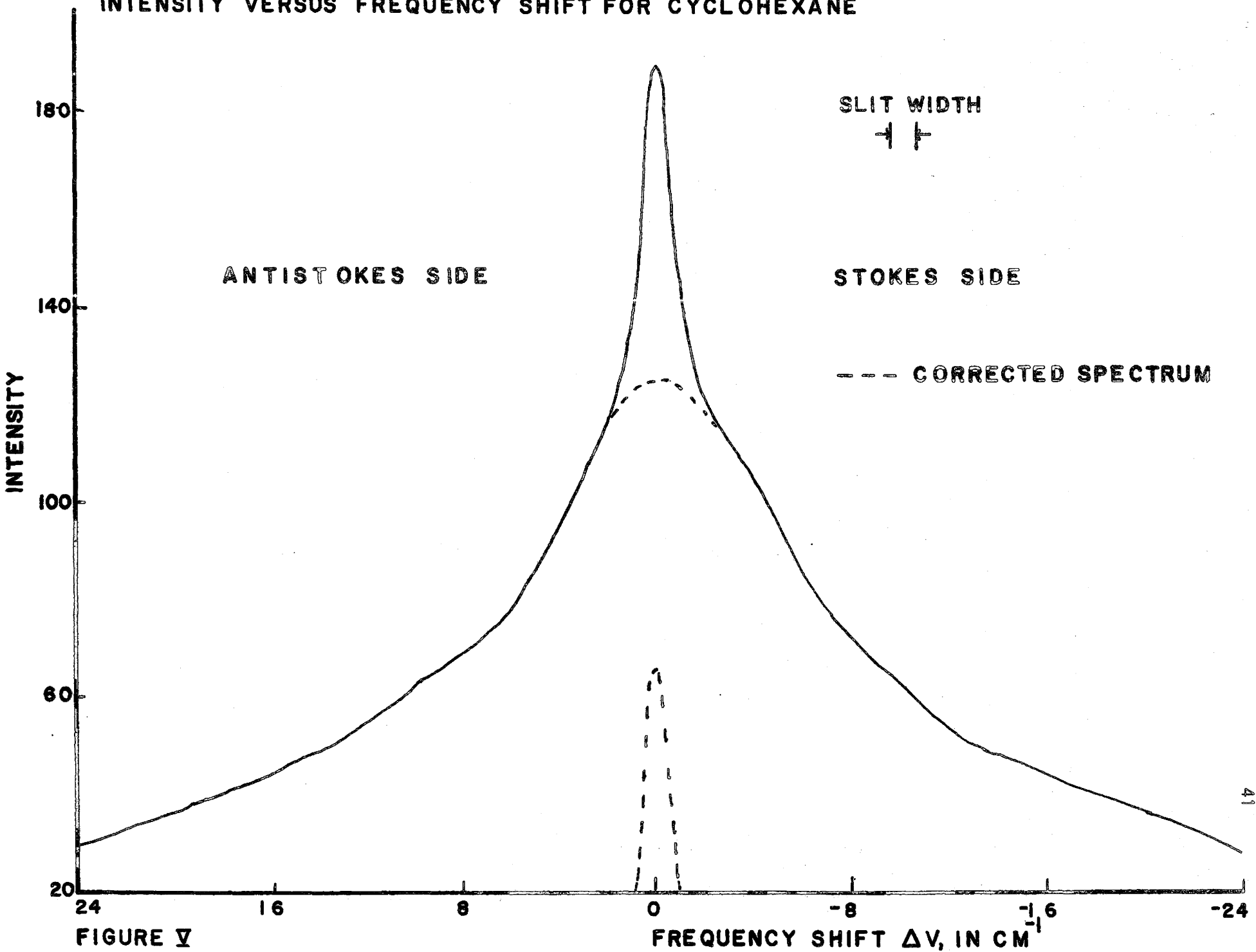
$$\sigma_R^O \sim \sqrt{2} \sigma_R^S$$

C_6H_{12} (figure V) illustrates the extrapolation procedure. The total intensity profile centered at zero frequency consists of a narrow line, with a F.W.H.M. determined by the spectrometer slit width, sitting on a much broader peak. As the spectrometer slit width was reduced, the narrow line contracted to widths close to the spectrometer slit widths, leaving the width of the background peak unchanged. It was concluded that the narrow line was due to one of the above four problems and did not simply represent a sharp increase in the depolarized intensity near zero frequency. For example, a vertical misalignment of the scattering cell by 1° is sufficient to account for the narrow component. The H.W.H.M. (σ_R^O) of the broad background with the collisional component (4/7 power used) removed was $8 \pm .5 \text{ cm}^{-1}$. The extrapolation prediction for σ_R^O is $9 \pm 1 \text{ cm}^{-1}$, in reasonable agreement.

V.5 Relative Intensity Ratios of the Collisional Component

Unfortunately, there is no theory available in the literature describing the integrated intensity ratios of the collisional component. As a result, a simple model based on a molecular frame distortion mechanism will be constructed and applied to all the liquids except $C_{14}H_{14}O_2$ and $C_6H_5NO_2$, which were difficult to analyze properly due to their asymmetric structure.

INTENSITY VERSUS FREQUENCY SHIFT FOR CYCLOHEXANE



The model assumes that when two molecules with relative velocity v collide, there is an angular distortion $\sigma(v)$ in the bond framework of each molecule. For small displacements (a few tenths of angstroms), the change in polarizability from the equilibrium state $\Delta\alpha$ is assumed to depend linearly on the angular displacement $\sigma(v)$ ^(53,54). Using the expression for the total scattered intensity (equation II-5), and since $\mu_a \propto \Delta\alpha$, the collisional intensity distribution becomes

$$I(c) = \int_0^{\infty} N(v,b) \Delta\alpha^2(v) dv \quad V-6$$

$$\therefore I(c) = \int_0^{\infty} N(v,b) \sigma^2(v) dv \quad V-7$$

The azimuthal angular proportionality constant in $\mu_a \propto \Delta\alpha$ affects the magnitude of the absolute intensity, but cancels out in an intensity ratio of similarly structured molecules. $N(v,b)$ is the number of collisions per unit volume per unit time with impact parameter b and is given by equation II-6. The expression for $N(v,b)$ is appropriate for gases but will serve as a first order approximation to the liquid state. Just as in Bucaro and Litovitz' theory for collision induced scattering, a zero impact parameter b will be assumed for the closely packed liquid state⁽⁵⁵⁾.

As is quite often the case in Chemistry, the chemical bonds are viewed as Hooke's law springs with spring constant k_s . When two molecules collide, their relative kinetic energy $1/2 \mu v^2$ is stored as potential energy

$1/2 k_{\sigma} \sigma^2(v)$ in the distorted springs and then returned as the distortion process relaxes. For the molecules studied in this experiment, the spring constants k_{σ} corresponding to the stretching and compressing modes were an order of magnitude greater than the angular spring constant k_{σ}/R_o^2 appropriate for the bending modes⁽⁵⁶⁾. It was therefore assumed that the predominate distortion mechanism was the bending of the atoms from their equilibrium positions in the molecule. For the tetrachlorides, with central atom X, the angular displacement of the Cl-X-Cl bond for collisions of molecules with relative kinetic energy of a few kT can be as much as 10° .

Using $\sigma^2(v) \propto \mu v^2/k_{\sigma}$ equation V-7 becomes

$$I(c) \propto n^2 \left(\frac{\mu}{kT}\right)^{3/2} (\mu/k_{\sigma}) \int_0^{\infty} v^5 e^{-\frac{\mu v^2}{2kT}} dv \quad V-8$$

This integral is easily evaluated using the C.R.C. Handbook of Mathematics and Physics.

$$I(c) \propto n^2 \left(\frac{\mu}{kT}\right)^{3/2} (\mu/k_{\sigma}) \left(\frac{\Gamma(3)}{2\left(\frac{\mu}{2kT}\right)^3}\right) \quad V-9$$

Defining an integrated collision intensity ratio $I_R(c) = I_1(c)/I_2(c)$, where subscripts 1 and 2 refer to liquid 1 and 2 respectively, then:

$$I_R(c) = \left(\frac{n_1}{n_2}\right)^2 \left(\frac{\mu_1}{\mu_2}\right)^{1/2} \left(\frac{k_{\sigma 2}}{k_{\sigma 1}}\right) \left(\frac{T_1}{T_2}\right)^{3/2} \quad V-10$$

Since $n = \rho/2\mu$, and for constant liquid temperatures, $I_R(c)$ reduces to the simple expression

$$I_R(c) = \left(\frac{\rho_1}{\rho_2}\right)^2 \left(\frac{\mu_2}{\mu_1}\right)^{5/2} \left(\frac{k\sigma_2}{k\sigma_1}\right)$$

V-11

The ratio of the integrated intensities of two molecular liquids based on a frame distortion mechanism, should vary as the ratio of the liquid densities squared, inversely as the 5/2 power of the reduced masses, and inversely as the angular spring constants.

Table VI lists the angular force constants and the bond lengths.

Table VII gives the calculated intensity ratios $I_R^{\text{calc.}}$ and the experimentally observed ratios $I_R^{\text{Exp.}}$ for pairs of similarly structured molecules. The agreement is quite good. The low calculated ratios for $\text{CCl}_4/\text{SiCl}_4$ and $\text{C}_6\text{H}_{12}/\text{SiCl}_4$ may be accounted for by the inclusion of the electron overlap scattering mechanism. Table I, column 4 indicates that CCl_4 has the lowest ionization potential of the tetrachlorides, while the ionization potential of C_6H_{12} is considerably lower than that of CCl_4 . On the assumption that the ionization potential is a measure of the deformability of the outer molecular electron orbitals, then CCl_4 , C_6H_{12} may have significant contribution from the electron overlap mechanism. Taking this effect into account might well improve the calculated ratios.

Very little more can be done until a complete theory is available predicting the exact proportion of the electron overlap and frame distortion mechanisms and predicting how each depends on the molecular parameters.

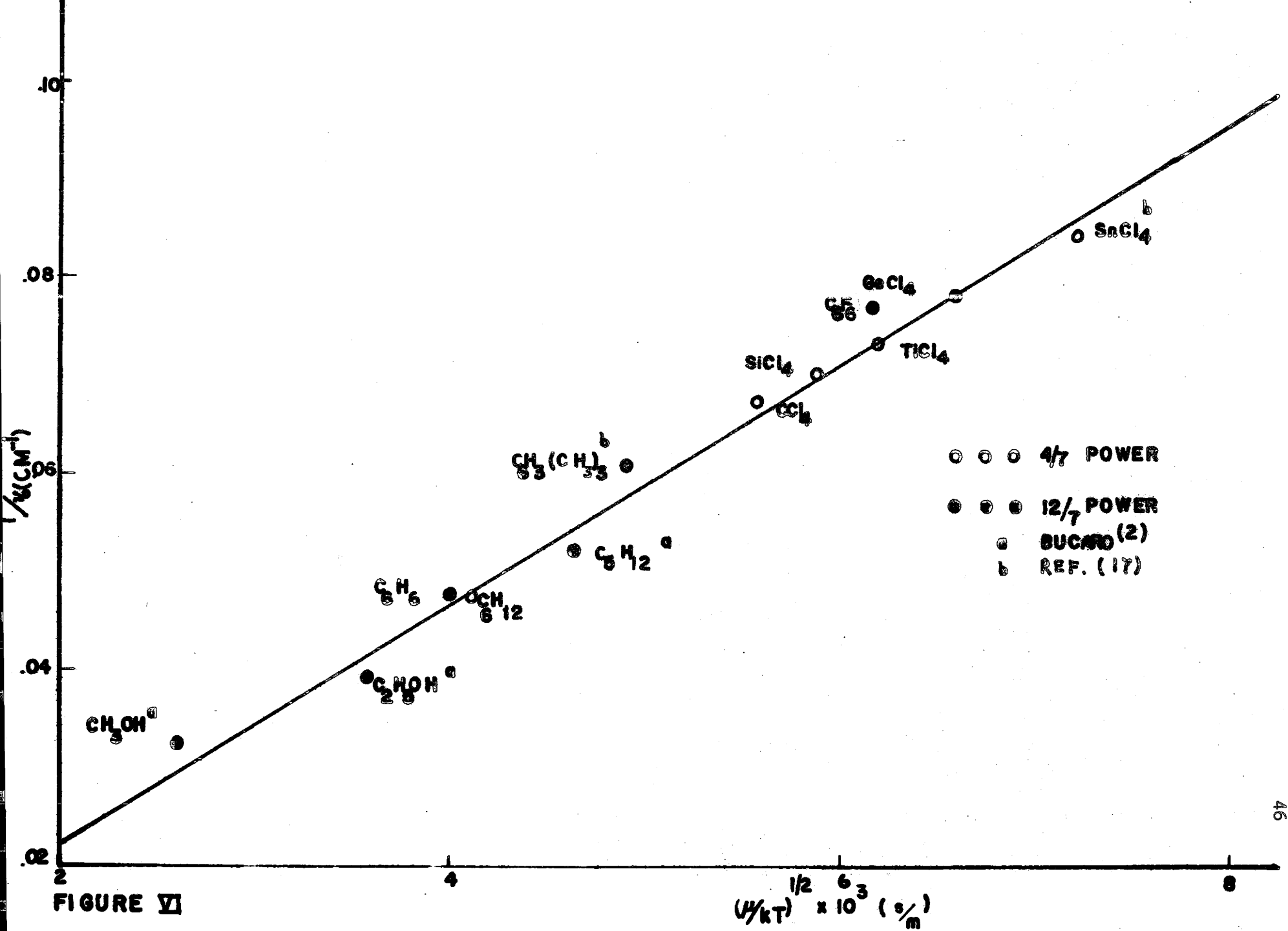
V.6 Collisional Linewidth

As outlined in Chapter II, the linewidth parameter $1/\nu_0$ is a measure

of the duration of a collision and has been successfully related to the term $(\mu/kT)^{1/2}$. H. Howard-Lock et al. interpreted the proportionality constant $2\pi\gamma_2^{-1}$ as being a measure of the distance between two colliding molecules for maximum induced anisotropy (equation II-9). In Hyung Kyu Shin's expression for $1/v_0$, the proportionality constant is just the Leonard-Jones radial parameter σ (equation II-14). Plots of $1/v_0$ versus $(\mu/kT)^{1/2}$ should provide an estimate of both γ_2^{-1} and σ . However, since $1/v_0$ depends on the nature of the scattering mechanism, the results are not expected to fall on one line. In fact, the graph of $1/v_0$ versus $(\mu/kT)^{1/2}$ for isotropic (4/7, 12/7) and anisotropic (4/7, 12/7) molecules yields three straight lines. The values of $1/v_0$ corresponding to the 12/7 power used for the isotropic liquids form the first line. The values of $1/v_0$ corresponding to the 4/7 power for the anisotropic molecules form the second line. Finally, the $1/v_0$ values corresponding to the 4/7 power for the isotropic molecules and the 12/7 power for the anisotropic molecules fall remarkably on a single third line, which lies between the first two. See figure VI. The values of (γ_2^{-1}, σ) for the three lines are $(.77\text{\AA}, 4.84\text{\AA})$, $(.58\text{\AA}, 3.64\text{\AA})$, $(6.5\text{\AA}, 4.1\text{\AA})$ respectively.

For liquids in which the Leonard-Jones potential is applicable, the parameter σ is representative of the molecular collision cross-section. Thus for the isotropic molecules (4/7 power), and anisotropic molecules (12/7 power), the collisional cross-sections are very similar. This fact was used in the calculation of τ_R in section V.4.

Nitrobenzene and benzyl benzoate do not fall on any of the three lines.



Benzyl benzoate can be brought significantly closer to the linear region if $\mu/2$ is used instead of μ in the $\mu^{1/2}$ expression, identical to the behaviour previously noted in section V.4. It may be concluded that this complex molecule behaves more like a simple benzene ring in collision-induced scattering. The discrepancy for nitrobenzene is probably due to the complete inadequacy of the Leonard-Jones potential in describing the intermolecular interaction between such asymmetric molecules.

The interpretation of the three lines is not clear. Since there is no conclusive preference from the curve-fitting results of the isotropic and anisotropic molecules to either $4/7$ or $12/7$ power, the results may be interpreted as follows: If the dominant mechanism in the isotropic molecules is frame distortion, the parameters (τ_2^{-1}, σ) would be $(.77\text{\AA}, 4.8\text{\AA})$, while if the dominant mechanism in the anisotropic molecules is electron overlap, the parameters would be $(.56\text{\AA}, 3.6\text{\AA})$. Finally, if the dominant process in the isotropic molecules is electron overlap and the dominant process in the anisotropic molecules is frame distortion, the parameters (τ_2^{-1}, σ) would identically be given by $(.65\text{\AA}, 4.1\text{\AA})$. Note, that for both isotropic and anisotropic molecules, the distance between two molecules for maximum induced anisotropy is smaller for the electron overlap mechanism than for the frame distortion mechanism.

The significance of only one set of parameters for isotropic molecules ($4/7$ power) and anisotropic molecules ($12/7$ power) is uncertain. It's tempting to conclude that the single set of parameters is somehow indicative of the trend to better χ^2/N (table IV, column 4) for the isotropic molecules

using the $4/7$ power and the anisotropic molecules with the $12/7$ power. However, further experimental and theoretical evidence is needed before any definite conclusions can be drawn about the proportion of each mechanism in isotropic and anisotropic liquids.

TABLE III

Curvefit values for the relaxational and collisional linewidth parameters (taken from 5 cm^{-1}), and their respective correlation times.

	σ_R^S cm^{-1}		τ_R $\times 10^{12} \text{ sec.}$		$\nu_O (\text{cor.})$ cm^{-1}		τ_C $\times 10^{12} \text{ sec.}$	
	4/7	12/7	4/7	12/7	4/7	12/7	4/7	12/7
SiCl_4	$5 \pm .3$	$6 \pm .4$	$1.1 \pm .06$	$.9 \pm .07$	$14.3 \pm .4$	$9.2 \pm .3$	$.37 \pm .01$	$.58 \pm .02$
GeCl_4	$5 \pm .2$	$6.5 \pm .3$	$1.1 \pm .04$	$.8 \pm .04$	$12.8 \pm .3$	$8.7 \pm .2$	$.42 \pm .01$	$.61 \pm .01$
CCl_4	$4.2 \pm .1$	$6.0 \pm .3$	$1.26 \pm .04$	$.9 \pm .05$	$14.9 \pm .4$	$9.9 \pm .3$	$.36 \pm .01$	$.54 \pm .02$
TiCl_4	$5.8 \pm .4$	$7.4 \pm .6$	$.92 \pm .06$	$.72 \pm .06$	$13.7 \pm .6$	$9. \pm .6$	$.39 \pm .02$	$.59 \pm .05$
C_6H_{12}	$6.5 \pm .3$	$8.5 \pm .4$	$.82 \pm .03$	$.63 \pm .03$	$21.2 \pm .4$	$14.1 \pm .3$	$.25 \pm .01$	$.38 \pm .01$
C_6H_6	$5.2 \pm .2$	$5.9 \pm .4$	$1. \pm .04$	$.9 \pm .06$	$31.5 \pm .1$	$21. \pm .5$	$.17 \pm .01$	$.25 \pm .005$
C_6F_6	$4.8 \pm .4$	$5.5 \pm .6$	$1.1 \pm .1$	$1. \pm .1$	$18.5 \pm .6$	$13.1 \pm .5$	$.29 \pm .01$	$.41 \pm .02$
$^{14}\text{H}_2^{16}\text{O}_2$	$5.1 \pm .5$	$6.5 \pm .7$	$1. \pm .1$	$.82 \pm .08$	$34.8 \pm .6$	$23.2 \pm .5$	$.15 \pm .002$	$.23 \pm .005$
$^6\text{H}_5^1\text{NO}_2$	$5.1 \pm .2$	$5.8 \pm .1$	$1. \pm .02$	$.92 \pm .02$	$31.5 \pm .6$	$20.2 \pm .3$	$.17 \pm .003$	$.26 \pm .004$

4/7, 12/7 refer to the power of the exponential weighting factor.

TABLE IV

Experimental (exp.) and curvefit (c. fit) values for the collisional linewidth parameter ν_0 .

	ν_0 (exp.)		ν_0 (c. fit)		ν_0 (c. fit)*		χ^2/N	
	cm. ⁻¹		cm. ⁻¹		cm. ⁻¹			
	4/7	12/7	4/7	12/7	4/7	12/7	4/7	12/7
<chem>SiCl4</chem>	14. ± .3	9.6 ± .2	14.3 ± .4	9.2 ± .3	--	--	.5	1.5
<chem>GeCl4</chem>	12.5 ± .2	8.6 ± .2	12.8 ± .3	8.7 ± .2	13.4 ± .3	9.1 ± .3	3.0	3.3
<chem>CCl4</chem>	14.4 ± .3	10.1 ± .3	14.9 ± .4	9.9 ± .3	15.6 ± .5	11.2 ± .4	1.7	1.9
<chem>TiCl4</chem>	13.7 ± .5	8.9 ± .5	13.7 ± .6	9. ± .6	--	--	1.6	2.0
<chem>C6H12</chem>	20.8 ± .3	14.3 ± .3	21.3 ± .4	14.1 ± .3	22.**	14.8**	1.3	1.2
<chem>C6H6</chem>	32.4 ± .7	21.5 ± .6	31.5 ± .1	21. ± .5	30.6 ± .6	20.8 ± .5	4.0	1.6
<chem>C6F6</chem>	19.2 ± .5	14.1 ± .4	18.5 ± .6	13.1 ± .5	17.2 ± .4	11.8 ± .4	2.0	1.2
<chem>C14H14O2</chem>	38.6 ± .5	23.2 ± .4	34.8 ± .6	23.2 ± .5	--	--	6.3	2.7
<chem>C6H5NO2</chem>	29.4 ± .5	20.3 ± .3	31.5 ± .6	20.2 ± .3	28.1 ± .4	19. ± .3	1.2	.9

* Curvefit values taken from 1967-1970 data using a Spex Spectrometer, .5 cm⁻¹ slits, and a 40 mw. He-Ne laser.

** Experimental values of ν_0 from ref. (2).

4/7, 12/7 refer to the power of the exponential weighting factor.

TABLE V

Depolarized relaxational and collisional integrated intensities ($I_V^H(b)$), starting from 5 cm^{-1} and relative to the 459 cm^{-1} line in CCl_4 .

	$I_V^H(T)$		$I_V^H(R)$		$I_V^H(C)$		$I^S(R)/I^S(C)$	
	4/7	12/7	4/7	12/7	4/7	12/7	4/7	12/7
SiCl_4	.42	.11	.15	.31	.27	1.5	2.7	
GeCl_4	.77	.28	.44	.49	.33	1.7	3.3	
CCl_4	.80	.17	.32	.63	.48	1.1	2.2	
TiCl_4	.83	.27	.44	.56	.39	1.3	2.5	
C_6H_{12}	1.0	.32	.49	.69	.51	1.9	3.3	
C_6H_6	15.	7.6	8.9	7.4	6.1	7.4	10.6	
C_6F_6	8.	5.2	6.2	2.7	1.8	7.7	12.	
$\text{C}_{14}\text{H}_{14}\text{O}_2$	9.	3.2	4.4	5.8	4.6	4.7	7.5	
$\text{C}_6\text{H}_5\text{NO}_2$	18.	10.2	11.8	7.8	6.2	10.	14.	

4/7, 12/7 refer to the power of the exponential weighting factor.

TABLE VI

Bending force constants (k_σ/R_o^2) and bond lengths (R_o)

	k_σ/R_o^2 *	R_o **	Bond	k_σ
	md/A°	A°		$\times 10^{11}$ ergs.
SiCl ₄	.059	2.02	Si-Cl	.24
GeCl ₄	.053	2.09	Ge-Cl	.23
CCl ₄	.103	1.77	C-Cl	.32
TiCl ₄	.037	2.19	Ti-Cl	.18
C ₆ H ₁₂	.425	1.09	C-H	.51
C ₆ H ₆	.09 ⁽⁵⁷⁾	1.09	C-H	.11 ^{***}
C ₆ F ₆	.07 ⁽⁵⁸⁾	1.3	C-F	.12 ^{***}

* Unless otherwise stated the values were taken from T. Shimanouchi, Pure Appl. Chem. 7, 131 (1963).

** Unless otherwise stated the values were taken from R. T. Sanderson, Chemical Bonds and Bond Energy (Academic Press, New York, 1971).

*** Out of plane bending mode.

TABLE VII

Calculated and experimental integrated intensity ratios for the collisional component ($I_V^H(c)$, from 5 cm^{-1})

Ratios (R)	$I_R^{\text{calc.}}$	$I_R^{\text{Exp.}}$
$\text{GeCl}_4 / \text{SiCl}_4$	.9	$1.2 \pm .1$
$\text{TiCl}_4 / \text{SiCl}_4$	1.4	$1.4 \pm .2$
$\text{CCl}_4 / \text{SiCl}_4$	1.1	$1.7 \pm .1$
$\text{C}_6\text{H}_{12} / \text{SiCl}_4$	.8	$2. \pm .2$
$\text{C}_6\text{H}_6 / \text{C}_6\text{F}_6$	3.5	$3.4 \pm .3$

CHAPTER VI

SUMMARY

The depolarized Rayleigh wing spectra of isotropic and anisotropic molecules were taken at room temperature using a Coderg double monochromator with 1 cm^{-1} entrance slits.

The experimental line profile was decomposed by least squares curvefitting techniques into relaxational and collisional components. Integrated intensities as well as depolarization ratios were found for each liquid.

The relaxational component was Lorentzian, had a linewidth that depended on $\mu^{3/2}/\rho$, and was interpreted as being a measure of the time between collisions τ_R . The excellent fits with the Lorentzian lineshape and linewidth dependence ($\tau_R \propto 1/\rho$) indicate that the relaxational component in the tetrachlorides may be described by the Lewis and Van Kranendonk intercollisional theory.

A simple model was constructed to predict the relative intensity ratios of similarly structured molecules based on a frame distortion mechanism. The results were in fair agreement with the model. The discrepancies in CCl_4 and C_6H_{12} indicated the necessity of including the electron overlap mechanism.

The collision linewidth parameter $1/(2\pi\nu_0)$ (sec.) was found to be proportional to $\mu^{1/2}$ with the proportionality constant representing the distance between two colliding molecules for maximum induced anisotropy. A single value of γ_2^{-1} of $.65 \pm .02 \text{ \AA}$ was obtained using the 4/7 weighting factor for the isotropic molecules and the 12/7 factor for the anisotropic molecules.

APPENDIX

Integrated Intensity of the Relaxational Component

Given

$$I(R) = I_R^S \left(1 + \left(\frac{v-S}{\sigma_R^S} \right)^2 \right)$$

Then

$$I_{\text{Total}}(R) = I_R^S \int_S^{\infty} \frac{dv}{1 + \left(\frac{v-S}{\sigma_R^S} \right)^2}$$

$$\text{Let } \left(\frac{v-S}{\sigma_R^S} \right) = \tan \theta$$

$$\therefore dv = \sigma_R^S \sec^2 \theta d\theta$$

$$\therefore I_{\text{Total}}(R) = I_R^S \sigma_R^S \int_0^{\pi/2} \frac{\sec^2 \theta}{1 + \tan^2 \theta} d\theta$$

$$\text{Since } 1 + \tan^2 \theta = \sec^2 \theta$$

$$I_{\text{Total}}(R) = I_R^S \sigma_R^S \int_0^{\pi/2} d\theta$$

and $\therefore$

$$I_{\text{Total}}(R) = \pi/2 (I_R^S \sigma_R^S)$$

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