RAMAN SPECTRA OF CERTAIN COLORED SUBSTANCES AND THE EXISTENCE OF AN OPTIMUM CONCENTRATION FOR MAXIMUM INTENSITY OF SCATTERED RADIATION

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ROBERT DWIGHT FISHER

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INTRODUCTION

Development of Raman Spectroscopy

The discovery of Raman spectra may be attributed to Sir C. V. Raman in 1928, thus the name Raman spectra. The Raman spectra of substances are similar to infrared absorption spectra in their connection with molecular vibrations but differ quite drastically from them in their mode of excitation.

It is well known that most transparent substances, such as gases and liquids, do not transmit light perfectly but scatter a small amount of it in all directions. The scattered light is polarized, and its spectrum contains all the wavelengths present in the source. However, Sir C. V. Raman discovered that a number of much weaker polarized and dipolarized lines also appeared in the spectrum. These lines are now called Raman lines. Raman lines have been found to be characteristic of the substances under investigation. The scattered light has a slightly different frequency from that of the original or incident light beam, and there is a change in the rotational or vibrational energy within the source molecule. This change in frequency is known as the Raman frequency shift.

This light scattering effect, as demonstrated by Raman, had been predicted from theoretical considerations before his experiment, and numerous investigators in Europe and the United States were searching for the frequency shifted lines. Interest in this phenomena had become widespread by the late thirties and early forties.

Research investigations have been carried out primarily by university scientists and trained spectroscopists in a few industrial laboratories. Widespread application of this technique has been hampered principally because of the difficulties associated with sample preparation, weakness of the scattered radiation, and the development of satisfactory sources of excitation. However, the relatively recent availability of suitable sources and recording spectrometers from the leading manufacturers has increased lately the use of the Raman technique.

Significance of Raman Spectra

Relation to Infra-red Spectra. The theory of the Raman effect shows that the Raman frequencies are closely related to frequencies of vibration within the molecule. When radiation interacts with a molecule, part of the energy of the exciting photon is in effect utilized by that molecule to excite a vibration, and the remainder escapes as a photon of energy that is lower by the amount taken up by the molecule. The frequency difference between the exciting and scattered radiation multiplied by Planck's constant, $h\Delta\bar{v}$, is equal to the energy of vibration of the molecule. Therefore, the shift in frequency of the lines is proportional to the vibrational-rotational energy involved in the transitions. Thus, Raman shifts should correspond to actual absorption bands appearing in the infrared spectrum of a compound since both are due to shifts in the vibrational-rotational levels of the molecule. The Raman spectrum is just as characteristic of a substance as the infrared spectrum. However, it must be remembered that all infrared frequencies do not have their Raman counterpart and vice versa. The selection rules governing the relations between molecular vibrations and the Raman and infrared frequencies can be found in numerous references, such as that of Herzberg (1) and Hibben (2). There is one important and easily remembered rule which might be mentioned. In molecules with a center of symmetry, molecular vibrations in which motion of the nuclei is symmetrical to the center of symmetry may be excited in Raman scattering and not by infrared absorption. Conversely, vibrations antisymmetrical to the center may be excited by infrared absorption but not in Raman scattering. This indicates that the study of the Raman spectrum supplies in many respects the same information concerning the rotational and vibrational energy levels about a molecule as the study of its infrared spectrum. From this is sometimes derived the vibrational frequency, force constants, moments of inertia, internuclear distance, and rotational frequencies.

Even for homonuclear diatomic molecules, which have no infrared spectrum, the rotational and vibrational constants can be derived with the aid of the Raman spectrum.

Relation to Inorganic Chemistry. The Raman effect enables one to distinguish between the two major types of chemical linkages, the covalent and electrovalent. Wherever the linking is of a covalent type, the Raman lines appear with relative large intensity while the reverse is the case when linkages of an electrovalent type occur. The fact that many organic compounds, which are characterized mostly by covalent linkages, exhibit prominent Raman spectra may be taken as further evidence to support the above conclusion. This close correlation between intensity of the Raman lines and the chemical nature of the linkage can be easily explained. The intensity of a Raman line is determined by two factors, the symmetry of the molecule and the extent to which its polarizability is affected by the oscillation in question. If the polarizability of a molecule is either totally independent of or very insensitive to variations in the nuclear distances, nuclear oscillations will cause little or no alteration in the polarizability and, consequently, will not give rise to Raman lines. This is likely to be the case when electrons have gone definitely over from one nucleus to the other in molecule formation (electrovalent). On the other hand, if the binding electrons remain common to the nuclei (covalent), the polarizability of the molecule will naturally be considerably affected by the positions of the nucleus, and nuclear oscillations will be accompanied by appreciable variations of the polarizability and, consequently, will give rise to Raman lines. Since Raman spectra are characteristic of the molecular structure, one would expect a change to occur in complex formation. Dipole associations are only a type of loose adherence of dipole molecules and usually do not result in the appearance of new Raman lines. However, the existing Raman lines are shifted or broadened very considerably. The association of the hydroxyl group of one molecule with the hydroxyl group of another through a coordinate link may be regarded as an example of coordination. The case of water, in which some of the Raman lines have been attributed to $(H_2O)_2$ and to $(H_2O)_3$ molecules, is probably an example of this type of complex formation.

The substitution of an isotopic atom instead of the original one in a molecule alters both the symmetry of the molecule and the effective mass. The former affects the selection rules, degeneracy and polarization factors whereas the latter alters the magnitude of the characteristic frequencies. Both of these consequences are manifested in the Raman spectra and offer a wide field of investigation. The above examples help to indicate the scope of Raman spectroscopy in the field of inorganic chemistry. However, there are many other applications of Raman technique in inorganic chemistry, such as in the study of water of crystallization, mixed molecules, and others.

Relation to Organic Chemistry. A study of the Raman effect has been of great value in the field of organic chemistry and has thrown considerable light on a variety of problems. Among the major problems in which it has been successfully utilized are: 1) the determination of the presence or absence of specific linkages in a molecule, 2) the qualitative identification of impurities of certain types, 3) the quantitative estimation of the relative proportions in which the constituents of a mixture are present, 4) the elucidation of the structures of important molecules, and 5) a study of different types of isomerism. The field of research and the results obtained are so vast that it is not desirable to consider this branch of the subject in detail.

Relation to Physical Chemistry. Certain aspects of the Raman effect have thrown considerable light upon such important problems in physical chemistry as: 1) the nature of the liquid state, 2) calculation of thermodynamic quantities, 3) change of state and dipole moments, 4) polymorphous crystals, 5) hydrolysis, 6) degree of dissociation, and 7) the common ion effect.

Application to Qualitative and Quantitative Analysis. For purposes of identification of an unknown substance by comparison of its Raman spectrum with recorded spectra, it is necessary to measure the Raman shifts of the unknown and at least to estimate their intensity order. For photographic work, the best practice is to measure the Raman band positions relative to an adjacent iron or argon comparison spectrum. A low power traveling microscope is usually used. Use of Raman spectra for analysis of mixtures is possible because the Raman lines of most substances retain their positions and relative intensities upon dilution. Thus, if several prominent lines of a known substance can be detected in a mixture, the presence of that substance is established.

Quantitative Raman spectroscopy has so far been applied to clear, liquid mixtures. In this field a number of experimental procedures and successful analyses have been described. Most of the quantitative work has been done with hydrocarbons.

Theory of Raman Scattering

The theory of Raman scattering is well known. However, a brief outline of the main theoretical principles should be presented.

The general principles upon which the theory of molecular scattering is based are that an incident electric field E produces an induced dipole which is $u_1 = a \times E$, where a is the polarizability of the molecule. It is now assumed that during the molecular vibration which proceeds the polarizability, a, undergoes a change about an equilibrium position. Expanding the polarizability in a power series, it may be expressed as : $a = a_{eq} + da/dx\ A\sin 2\pi v_{vib}t$. The incident electric field produces an oscillating electric moment $E_o \sin 2\pi vt$. It is now assumed that during the molecular vibration which proceeds with the frequency v', the polarizability, a, suffers a small change having the same frequency. The variation of the induced dipole moment with time is given by the following:

$$u_i = a_{eq}E_o \sin 2\pi vt + \tfrac{1}{2} da/dx A E_o \left[\cos 2\pi(v'-v_{vib})t - \cos 2\pi(v'+v_{vib})t\right]$$

According to the above equation, the induced dipole moment oscillates not only with the frequency v' of the incident light, but also with the frequencies $v' - v_{vib}$ and $v' + v_{vib}$. These terms are smaller and larger respectively than that of the incident light by an amount equal to the vibration frequency of the diatomic molecule. The first term of the oscillating dipole gives rise to scattered radiation of the same frequency as the incident light, that is, Rayleigh scattering. The second term constitutes the Raman effect. The scattered radiations having these frequencies are, respectively, the Stokes and anti-Stokes lines. According to this formula, the two frequencies, $v' - v_{vib}$ and $v' + v_{vib}$, should appear with equal intensity. This prediction has not been verified by experiment. The frequency $v' - v_{vib}$ appears almost always with greater intensity. This line is called the Stokes line. This may be explained by the fact that at room temperature most molecules are in their ground state, and the probability of a photon colliding with ground state molecules is much greater than that of colliding with molecules in an excited state.

Advantages and Disadvantages of Raman Spectroscopy

There are certain advantages and limitations of the Raman technique as a tool for chemical investigations. Briefly, these are as follows:

Advantages

1. A complete vibrational spectrum is obtained.
2. Aqueous solutions can be used in Raman spectroscopy whereas in the infrared this must be avoided.
3. A low frequency vibrational spectrum is obtained whereas in the infrared it is very difficult to work in this region (250--50 cm^{-1}) due to the lack of suitable instruments.
4. Raman spectroscopy enables one to study inorganic compounds and large molecules with relative heavy atoms which give rise to low frequencies.
5. The occurrence of a Raman spectrum depends on the polarizability of the molecule but is independent of a permanent dipole moment. Thus, a Raman spectrum for molecules that have no infrared spectrum can also appear.
6. Photographic techniques can be employed as well as photoelectric recording.

Disadvantages

1. Samples must be absolutely pure and free of contamination of any kind, including dust particles.

2. It is difficult to obtain Raman spectra of highly colored compounds which absorb radiation.
3. The scattered radiation is weak.

Purpose of This Thesis

The Raman spectra of a compound is inherently weak. In order to obtain a satisfactory spectrum the intensity of each Raman line should be as great as possible. In general the relative intensity of a Raman line is inversely proportional to the 4th power of the wavelength of the scattering radiation. It is, therefore, desirable to use excitation with short wavelengths, such as the mercury 4047 A° or 4358 A° line. However, for colored compounds, the intensity of scattering does not depend upon the fourth power factor. A colored compound will absorb certain radiation of specific wavelengths in the visible region of the spectrum. Since Raman scattering depends upon the scattering of light by molecules and not by absorption of light, difficulties of obtaining such spectra have been encountered. In fact, Raman spectroscopy has been limited thus far to clear or very slightly colored liquid mixtures. The purpose of this research was to investigate the spectra of certain absorbing substances and to describe in detail methods of obtaining satisfactory spectra of such compounds as iron bis cyclopentadienyl and cyclooctatetraene. Also, it was tc postulate a reasonable explanation for the peculiar behavior of the Raman line with respect to concentration.

PRELIMINARY EXPERIMENTATION

Discovery of Ferrocene

The current discovery of the unusual compound, iron bis cyclopentadienyl has prompted the investigation of its physical, chemical, and structural properties. Ferrocene, or iron bis cyclopentadienyl, was discovered late in 1951 independently but at nearly the same time by Miller, Tebboth, and Tremaine (6) in England and by Kealy and Pauson (3) in the United States.

In 1952 Wilkinson, et al, (8) agreed on a sandwich structure of the molecule in which the iron atom and cyclopentadiene rings would be neutral, and the iron atom would have an effective atomic number of 36 (Krypton structure).

Raman Spectrum of Ferrocene

Since Raman spectra are characteristic of the structure of the molecule under investigation, various attempts were made to obtain clear cut Raman spectra. After many exhaustive attempts, a satisfactory Raman spectrum was accomplished by Lippincott and Nelson (4). This discovery further substantiated the structure proposed by Wilkinson. Difficulties encountered with obtaining the spectrum of this compound were due mainly to its color, and thus, absorption of the exciting radiation occurring and producing no Raman lines at all or very weak lines. Fortunately, for most nonpolar and many polar substances the intensity of a Raman line is directly proportional to the concentration. Therefore, the investigators assumed that if the concentration of the ferrocene in the Raman tube was increased, the intensity should increase correspondingly. However, this relationship did not prevail for if the concentration of the sample was increased, the intensity of the Raman lines decreased appreciably.

EXPERIMENTAL TECHNIQUE

The Raman Spectrograph

Raman spectra were obtained using a Hilger Raman spectrometer (Hilger & Watts Ltd., London). (Plate I, Appendix). This spectrograph is a prism type instrument and meets the two main requirements, speed combined with moderate dispersion, for Raman spectrography. For photographic work the speed of a spectrograph is inversely proportional to the square of its camera aperture (ratio of the lens diameter to its focal length). The Hilger spectrograph has an aperture of about f/5.4 in contrast to the f/12 to f/24 apertures of the usual emission spectrographs. Because of the natural width of the Raman lines themselves, a resolving power of 0.5 to 1.0 A° (2.5 to 5 cm^{-1}) in the 4358 A° Raman region is desirable. It is also desirable to have a recipricol dispersion in this region of about 20 A°/mm in order to permit the use of fast photographic emulsions without loss of overall resolution.

Source of Excitation

The mercury arc is practically the only source for the visible and ultraviolet regions that emits a simple high intensity line spectrum suitable for Raman work, although lamps of helium, cadmium, sodium and other elements have been tried. Since the intensity of

Raman scattering is roughly proportional to the fourth power of the frequency of the exciting line, the 2537 A° mercury line is very effective for excitation. Unfortunately, many organic compounds either absorb at this wavelength or are photochemically decomposed. Therefore, the 4047, 4358, or 5461 A° lines are used instead. The 4358 excitation is by far the most used.

The Hilger spectrograph used four low pressure mercury vapour lamps. These lamps were housed in a cylindrical water-cooled chamber. The lamps were symmetrically placed vertically around the sample tube which was placed on the axis of the cylindrical lamp housing. (Plate II, Appendix). The inside of the lamp housing was coated with magnesium oxide. The reflection of the 4358 A° mercury lines by magnesium oxide was above 99 percent. Thus, a ray of this wavelength could be reflected by the oxide over 100 times before 50 percent absorption took place. Therefore, the sample tube was irradiated very efficiently.

The excitation wavelength for ferrocene was 5461 A° Hg line, whereas, that for cyclooctatetraene was 4358 A°. These wavelengths were chosen since they were near or in the absorption bands of each compound. Experience has shown that the intensity of scattered radiation of colored compounds is not proportional to the 4th power of the exciting frequency. This is because one cannot neglect the factor expressed by $1/(v_0{}^2 - v^2)$ in the Rayleigh scattering formula. This factor may predominate since this work was done with material which absorbed near the exciting frequency. Therefore, this factor may become quite large and offset the $1/\lambda^4$ factor. If this is true, one would expect experimental verification or at least experimental evidence which would support this interpretation.

Cell and Cell Holder

The cell holder consisted of two compartments which surrounded the Raman cell providing for a filter, solution and water circulation to protect both filter and sample from the heat of the lamps. (Plate III, Appendix).

The Raman cell was made of a Pyrex glass cylinder with a flat Raman window sealed to one end. The opposite end of the cell was masked above the cell holder. This masking prevented direct reflection of incident mercury radiation into the spectrograph since, otherwise, the spectrum of even the best arcs would obliterate the weak Raman lines.

Filters

In Raman spectroscopy monochromatic radiation is desired. Filters are necessary to obtain monochromatic radiation and to reduce photodecomposition and fluorescence, if present, due to ultraviolet radiation emitted by the mercury lamps. Besides ultraviolet lines, the mercury arc emits strong lines at 4047 A° in the violet, 4358 A° in the blue, and also weak lines at 4348 and 4339 A°, a rather weak line at 4916 A°, and strong lines at 5461 A° in the green, and 5769 and 5790 A° in the yellow. All of the above lines are available for excitation, but the 5461 A°, 5770-90 A°, 4047 A°, and 4358 A° lines are the strongest. The advantages and disadvantages of these various lines when used as excitation sources, and the filters which can be used satisfactorily are summarized as follows.

If one chooses as his excitation source the Hg 5461 A° line, a saturated solution of potassium chromate is sufficient for filtering out the wavelengths below this line. A saturated solution of neodymium chloride is satisfactory for filtering out wavelengths above this excitation line. This line is particularly effective because it is an intense line and does not have any nearby components to produce shadows. In this respect it is far superior to the 4358 A° line where the nearby lines 4348 and 4339 A° produce shadows. These filters are excellent for removing the yellow doublet.

For excitation with the Hg 5770-90 A° doublet, a saturated solution of sodium dichromate is suitable for removal of the high frequency radiation. However, a water solution of the dye, cyannosine, is more effective in absorbing the intense 5461 A° Hg line. For wavelengths above the 5770-90 A° doublet, a solution of nickel sulfate is particularly effective in eliminating the weak Hg lines in this region although a better filter is desirable because the nickel sulfate solution also partially absorb the 5770-90 A° doublet. Excitation with this doublet is not as effective as with the 5461 A° line because the observed Raman spectrum will appear double (separation is about 64 cm^{-1}) because of excitation by both Hg lines, the difficulty of filtering out long wavelength radiation without absorbing or reducing the intensity of the yellow doublet, and the difficulty of filtering out the intense 5461 A° line. If it is absolutely essential to use yellow excitation, an improved source such as sodium or helium excitation is advisable.

If the excitation source is the 4358 A° line, the suitable filters are sodium nitrite for filtering out the lines below 4358 A°, and a Rhodamine dye is satisfactory to reduce the continum above

4400 A°. The 4358 A° line is a good source.

Photographic Technique

Plates. The photographic technique is very important in Raman spectroscopy. It can be used principally because it is cumulative and extremely weak radiations may be recorded by prolonged exposure.

Photographic plates differ in speed, constrast, spectral sensitivity, graininess of the image, and resolving power. For quantitative spectroscopic purposes, it is necessary to know how the response of the emulsion is affected by the intensity constancy and continuity of the incident light. It is generally assumed that the response of the plate depends only on the total energy per unit area which strikes the emulsion. Therefore, the exposure is defined as the product of the intensity and time during which the radiation acts, that is, $E = It$. This is known as the reciprocity law. Exposure may be varied by keeping the time constant and varying the intensity, or by keeping the intensity constant and varying the time, or varying both the time and intensity, or by making the intensity either intermittent or non-intermittent. However, when exposure is thus varied, identical blackening effects for equal exposures are not obtained. This phenomena is especially noticeable at very low or high intensities. This is termed the failure of the reciprocity law. At low intensities the exposure, required to produce a given photographic density, may be several times that required at higher intensities. In photographing very feeble sources, such as Raman spectra, a fast plate with small low intensity reciprocity failure should be selected. It is obvious that any ordinary photographic plate is not suitable for Raman spectroscopy. Therefore, the spectrum was recorded on 103 AE bkd. or 103 J bkd. Eastman Kodak photographic plates.

Development. Photographic development is essentially the reduction of the activated silver halide grains of the latent image to metallic silver. All manufacturers of plates and films usually supply formula for developers recommended for use with their emulsion. Since Raman lines are relatively weak, a high contrast developer is necessary. The developer used in this work was Kodak Formula D 19. For consistent results in photometric work, the development time, agitation of the solution during development, rinsing, and fixing time were identical in every respect after each successive operation.

Preparation of Samples

In Raman spectroscopy purity of the sample under investigation is of the utmost importance. Traces of contaminants from corks, rubber, stopcock grease, and similar items will produce sufficient continum to mask the weak Raman lines.

The ferrocene used in this research was prepared in the Kansas State College laboratory by the action of cyclopentadienyl magnesium bromide on ferric chloride. The cyclooctatetraene was obtained from Professor Arthur Cape of the Department of Chemistry, Massachusetts Institute of Technology.

Ferrocene was purified by repeated crystallization from acetone followed by vacuum sublimation. An apparatus was devised to insure purity of the sample by vacuum distillation of the sample into the

Raman tube before introduction of the solvent. This apparatus was previously cleansed thoroughly using hot nitric acid, repeatedly rinsed with distilled water, and then finally rinsed with acetone. It was then dried and all acetone and water vapour removed by means of a vacuum. Benzene was used for a solvent and introduced into the apparatus after releasing the vacuum. The solvent was then frozen, a vacuum produced, and the solvent then distilled directly into the Raman tube. Care must be taken, when removing the Raman tube by sealing off under vacuum, that the heat of the flame (torch) does not decompose any solvent in the vapour phase and thus contaminate the sample. This may be prevented by partially freezing the contents of the Raman tube before removing it from the apparatus. It is also essential to prevent the development of sufficient pressure, which might cause the tube to break, by gradual warming of the contents to room temperature.

Determination of Raman Intensities

The quantitative determination of intensities from spectral lines involves a means of measuring the density of the photographic line. Some type of photometer is generally used to measure the amount of light transmitted by the silver deposit, and if the area to be measured is that of a small slit or aperture, the instrument is called a microphotometer or microdensitometer. Density measurements were determined by means of a Leeds & Northrup recording microphotometer. In this instrument, the plate is traversed by a beam of light from a constant light source, and an inked record of the deflections of the indicating device of an automatic recording potentiometer is obtained on a wide paper strip. From this paper the photographic density is computed. The measurements required are d, the clear plate reading, d', the reading through the area photometered, and d_o, the full opaque or dark reading. Then,

$$\text{Density} = \log_{10} \frac{d - d_o}{d' - d_o}$$

By plotting the density against the $\log_{10}$ exposure time, a calibration curve is constructed. Various methods for obtaining such a calibration curve were investigated. The first method, and the most popular one, is by means of a sector or log sector disc. The rotation of this disc in front of the slit permits intermittent exposures to be taken. However, for precise determinations this method was not good since the steps produced by the disc are not pronounced nor distinct enough to be distinguished by the microphotometer. The second method, which proved to be more satisfactory, varied the time of exposure for individual spectra of the Hg excitation and produced various photographic densities.

EXPERIMENTAL RESULTS

The Raman spectra of ferrocene and cyclooctatetraene were obtained over a wide range of concentration values. The respective excitation frequencies for ferrocene and cyclooctatetraene were the 5461 A° and 4358 A° Hg lines.

Absorption coefficients were determined for every ten wavelengths throughout the visible spectrum with a known concentration of sample. The absorbancy indexes were calculated by means of the well known Beer-Lambert Law. The same procedure was followed for cyclooctatetraene except the ultraviolet region of the spectrum was used. The visible and ultraviolet spectra were obtained with a Beckman quartz spectrometer. These predetermined indexes were then used to determine the concentration of the sample under investigation by running an absorption spectrum of the sample. Both spectra were obtained from the same spectrometer in order to cancel out errors which might arise due to the use of different instruments.

The best Raman spectra of colored substances are obtained if one uses excitation frequencies which are near but not in an absorption band. This evidence is best illustrated by cyclooctatetraene which absorbs strongly near 4000 A°, but satisfactory spectra can be obtained using the 5461 A° Hg line even though it is near the absorption band.

Experimental evidence has shown that usable Raman spectra can be obtained for colored compounds where not only the exciting radiation but also the Raman scattering are being absorbed. This is illustrated by ferrocene which absorbs at wavelengths of 5000 to 6000 A°. Satisfactory Raman spectra can be obtained also by using the 5461 A° Hg line as an excitation source. Therefore, one may work in an absorption band if the absorption is not too intense.

Experimentally, it was found that the intensity of the Raman scattering for ferrocene and cyclooctatetraene seemed rather sharply dependent upon the concentration of the sample under investigation. To observe exactly how the intensity varied the relative intensity of the 1105 cm^{-1} Raman line for ferrocene and the 1651 cm^{-1} Raman line for cyclooctatetraene were plotted as a function of their concentration. It was seen that for a given wavelength there existed an optimum concentration for maximum intensity of scattering. This was considerably less than that of a saturated solution. (Plates IV and V, Appendix). Here the 1105 cm^{-1} ferrocene Raman line was far more intense when obtained from a benzene solution at a concentration of 0.18 moles/liter than when it was obtained at a concentration of 0.45 moles/liter. The effect was also apparent in the benzene 1178 cm^{-1} Raman line as well as in the Hg 5790 A^{o} line. (Plate VI, Appendix). For the ferrocene 1105 cm^{-1} line, it was found that the optimum concentration was near 0.25 moles/liter. The optimum concentration was different, of course, for each Raman line, and it was least for the low frequency Raman lines. Similar results were obtained with cyclooctatetraene except the optimum concentration was found to be in the range of 1.25 moles/liter instead of 0.25 moles/liter for ferrocene. (Plates V and VII, Appendix).

The intensity differences between the optimum concentration value and other concentration values of ferrocene and cyclooctatetraene were much greater than one would expect. The curves were very sharp, and the maximum intensity value was well defined since the peak was not broad. Therefore, at low concentrations of ferrocene or cyclooctatetraene, the Raman spectra were weak as expected. At high concentrations the Raman spectra were so weak that they could not be seen on the photographic plates. Thus, to obtain satisfactory spectra of a colored solution, one should use the optimum concentration value of that particular solution under investigation. This is necessary because the optimum concentration value produces maximum intensity.

A benzene solution was used in this work since it furnishes a

Raman line near 1178 cm^{-1} and is comparable in intensity to the 1105 cm^{-1} ferrocene line. It offered a means of testing any theoretical equation which might represent a solution to this phenomena since the intensity here should vary in some what the same manner as the intensity of the 1105 cm^{-1} Raman line.

A number of difficulties were associated with this research. There was the necessity for long exposure, variation in background from sample to sample, and the difficulty of obtaining a suitable calibration curve.

THEORETICAL INTERPRETATION

The experimental results may be explained or partially accounted for by the partial absorption of the exciting radiation before scattering followed by the partial absorption of the Raman radiation after scattering. A mathematical treatment can be attempted to describe the experimental results by the consideration of the geometry of the system. First, consider the scattering along the length of the Raman tube. It was assumed that the change in intensity was due to a decreasing increment caused by absorption and an increasing increment caused by additional scattering.

The intensity of the scattered light is proportional to the concentration of the sample, area irradiated, length of the cell, and the intensity of the incident light.

$$I_s = KAI_oCL$$

where K = constant
A = area
I_o = intensity of incident radiation
C = concentration
L = length of the cell

thus, $$\frac{dI_s}{dL} = KAI_oC$$

$$dI_s = KAI_oCdL$$

The change in intensity due to absorption is obtained from the Beer-Lambert Law, which in differential form is:

$$dI = I_s'KCdL$$

where K = constant
C = concentration
I_s' = intensity of incident radiation absorbed
L = length of the cell

The expression for the total intensity of scattered radiation will then be given by:

$$dI_s' = dI_s - dI$$

Therefore, $$dI_s' = KAI_oCdL - I_s'KCdL$$

then,

$$\int_0^{I_{out}} \frac{dI_s'}{KAI_o - I_s'K} = \int_0^L CdL$$

then,

$$I_{out} = \frac{KAI_o(1 - e^{-KCL})}{K}$$

From this equation it follows that there can be no optimum concentration for effective Raman scattering if I_o is not a function of concentration because the factor $(1 - e^{-KCL})$ has its maximum value only when C goes to infinity. Thus, the experimental observation of the existence of an optimum concentration means that the exciting radiation before scattering is the factor which determines whether one obtains or does not obtain Raman spectra of colored substances.

Therefore, we must consider the scattering not only along the length of the cell but also along the radius of the cell. According to the Beer-Lambert Law, scattering along the radius can be expressed as:

$$\frac{I_o}{I_{oo}} = e^{-K'RC}$$

$$I_o = I_{oo}\, e^{-K'RC}$$

Substituting this value into the previous equation, one obtains another expression for the intensity of scattering:

$$I_{out} = AI_{oo}\, e^{-CK'R} \quad (1 - e^{-CKL})$$

The factor derived from the intensity of scattering along the radius allows for the absorption of radiation before scattering. The optimum concentration may be expressed by differentiating the equation with respect to C and setting the result equal to zero. When this is done, the equation becomes:

$$C_{opt.} = \frac{1}{KL} \ln \left[1 + \frac{KL}{K'R} \right]$$

It must be mentioned that K' is the absorbency index (extinction coefficient) for the excitation radiation, and K is the absorbency index (extinction coefficient) for scattering radiation. Therefore, for every compound there is a different optimum concentration. For ferrocene the predicted optimum concentration at 1105 cm^{-1} above the Hg 5461 A° line is approximately 0.15 moles/liter. The experimental optimum concentration value was 0.25 moles/liter. The optimum concentration for cyclooctatetraene at 1650 cm^{-1} above the Hg 4358 A° line occurred experimentally at approximately 1.2 moles/liter while the predicted value is 0.30 moles/liter. Obviously, the theoretical equation does not predict accurately the optimum concentration values for either of these two compounds. A comparison of the predicted relative intensity with the experimental curves are shown in Plates IV, V, VIII, and IX, Appendix.

The author also investigated the effect of a change of radius of the Raman tube on the optimum concentration. The observed increase in intensity was consistent with the above equation. However, the scattering from the walls of the Raman tube imposed a limit on the size of the tube for which one may obtain satisfactory spectra. In any case the observed difference in intensity did not seem to warrant special effort to use small Raman tubes.

In an attempt to derive other equations which would correlate with experimental results, the following simplified situations were investigated.

The scattered radiation can be calculated from the average of the intensity of the radiation passing through the Raman tube normal to its surface. In this assumption the effective exciting radiation will be given by the following:

$$I_o = I_{av.} = \frac{I_s\,(1 - e^{-K'C2R})}{K'CR}$$

Substituting,

$$I_{out} = \frac{AI_o\,(1 - e^{-K'C2R})\,(1 - e^{-KCL})}{EE'CR}$$

The scattered radiation can be calculated from the average of the intensity of the radiation which is passing through the Raman tube. The average intensity of the effective exciting radiation will be given by the following:

$$I_o = I_{av.} = 2\,I_o\left[1 - \frac{(K'C2R)}{2\cdot 2\,!} + \frac{(K'C2R)^2}{3\cdot 3\,!} - \frac{(K'C2R)^3}{4\cdot 4\,!}\right]$$

Substituting,

$$I_{out} = 2\,I_o\left[1 - \frac{(K'C2R)}{2\cdot 2\,!} + \frac{(K'C2R)^2}{3\cdot 3\,!} - \frac{(K'C2R)^3}{4\cdot 4\,!}\right](1 - e^{-KCL})$$

The three curves representing these three theoretical equations can be seen in Plates VIII, IX, and X (Appendix), respectively.

When one compares the experimental and theoretical curves, it is obvious that the general shapes are not similar. The theoretical curves are too rounded, and the optimum concentration is reached too soon in all cases. Even though the theoretical equations do not agree with experimental results, they suggest a plausible reason for the incompatability of theory and experiment. The fact that the experimental curves are much steeper than the theoretical curves suggests that molecules may be present with abnormally high absorbitivity which was not taken into consideration in the theoretical explanation. A species with high absorbitivity would account for the steepness of the experimental curves and would explain possibly just why the theory was not similar to the results. It also must be remembered that colored compounds absorb radiation. This, of course, means that some of the molecules are being raised to higher electronic energy levels. Since they are in higher energy levels, their absorbitivity is increased, and this causes an increase in the extinction coefficient (absorbency index) which was used in the theoretical equations. In order to check this hypothesis, the following experiment was performed. Two spectra were obtained, the first with an exposure of one hour and the second with an exposure of one-half hour but with the intensity doubled. Theoretically, one would expect that both spectra should have the same intensity providing the Law of Reciprocity holds, and one has reason to believe that it does. However, the spectrum with the exposure of one hour was one and one-half times more intense than the other. Therefore, the intensity of the incident radiation has a definite effect upon the relative intensity of the line produced. This suggests that there exists in solution a concentration of electronically excited molecules that have high absorbitivity and cause a decrease in the intensity of a given line.

SUMMARY

Experimental evidence was obtained illustrating that the intensity of scattered radiation of a colored compound near an absorption band is equal to and in many instances larger than the scattering intensity one would obtain with colorless compounds. It may be stated definitely that an optimum concentration does exist for maximum intensity of spectra for the colored compounds investigated.

Experience has shown that one is hampered by the following factors: 1) absorption of the exciting radiation before scattering by the solution having extinction coefficient E', 2) absorption of the scattered radiation by the solution which at a given wavelength will have extinction coefficient E, and 3) finite concentrations of electronically excited molecules which are in solution and have high absorbitivities.

The technique demonstrated here will enable one to obtain satisfactory Raman spectra of a number of colored compounds. Indeed, it is now possible to study the Raman spectra of a number of colored and absorbing substances which have not been studied previously. Therefore, new information about their structural characteristics will now be made available through the interpretation of their spectra.

SUGGESTIONS FOR FURTHER WORK

A new field of research has been made available through the technique of studying Raman spectra of solutions at an optimum concentration, and many new compounds can now be investigated. This, of course, should be carried out, and the optimum concentration determined for other colored compounds.

The theoretical interpretation is in dire need of improvement, and research is open in this field of endeavor. The hypothesis that electronically excited molecules may exist in solution should be investigated much more thoroughly. Also, different sources of excitation such as sodium lamps should be used to investigate this effect.

Other Raman lines should be measured quantitatively. Indeed, the complete spectrum might be measured and the intensity versus concentration relationship developed for the entire spectrum.

The position of the Raman tube and lamps may play some importance in this effect. Also, the number of lamps used may be varied. In this research four lamps were used. It would be of interest to see if the optimum concentration decreases when only one lamp is used, or one could use the other extreme and employ five or six lamps. There are many other possibilities for further work, and indeed this research has raised a number of questions which can be answered only by further research.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Ellis R. Lippincott for guidance throughout this research. His directions for obtaining actual experimental data and contributions toward the interpretation of the experimental data were most valuable.

Aid in the form of a graduate assistantship furnished by the Department of Chemistry is gratefully acknowledged.

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APPENDIX

EXPLANATION OF PLATE I

Hilger excitation unit.

A. Height adapter
B. Prism and lens assembly
C. Clamp screw
D. Prism and lens adjuster

PLATE I

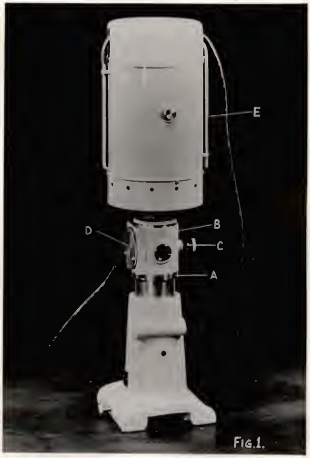
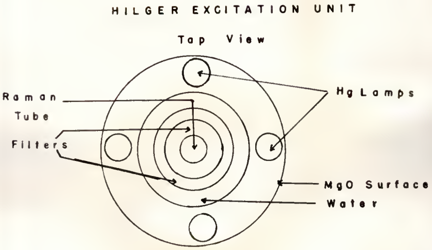


FIG. 1.

EXPLANATION OF PLATE II

Schematic drawing of excitation unit showing positions of lamps and sample.

PLATE II


HILGER EXCITATION UNIT
Tap View
Raman Tube
Filters
Hg Lamps
MgO Surface
Water

EXPLANATION OF PLATE III

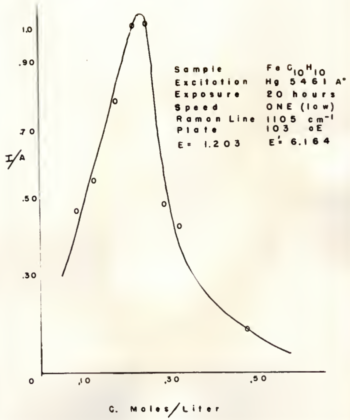
Hilger cell holder, cell, and lamp.

PLATE III

EXPLANATION OF PLATE IV

Experimental curve illustrating relationship between concentration and intensity of the 1105 cm^{-1} Raman line for ferrocene.

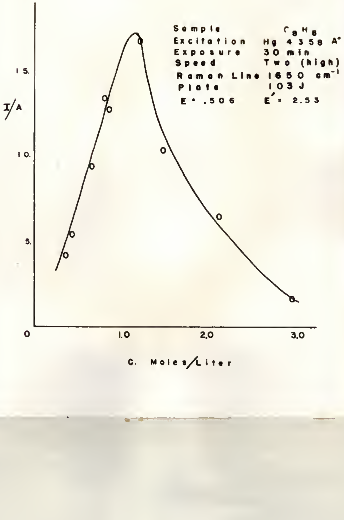
PLATE IV


1.0
.90
.70
I/A
.50
.30
0
.10
.30
.50
C. Moles/Liter
Sample Fe $C_{10}H_{10}$
Excitation Hg 5461 A°
Exposure 20 hours
Speed ONE (low)
Ramon Line 1105 cm^{-1}
Plate 103 oE
E= 1.203
E'= 6.164

EXPLANATION OF PLATE V

Experimental curve illustrating relationship between concentration and intensity of the 1650 cm^{-1} Raman line for cyclooctatetraene.

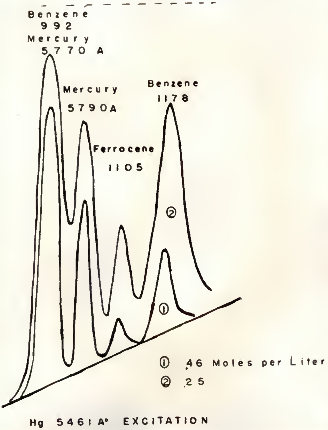
PLATE V


Sample C8H8
Excitation Hg 4358 A°
Exposure 30 min
Speed Two (high)
Raman Line 1650 cm-1
Plate 103J
E = .506 E' = 2.53
I/A
15.
10.
5.
0
1.0
2.0
3.0
C. Moles/Liter

EXPLANATION OF PLATE VI

Excerpt from densitometer showing curves illustrating relative densities of 1105 cm^{-1} Raman line with concentrations.

PLATE VI


Benzene
992
Mercury
5770 A
Mercury
5790A
Benzene
1178
Ferrocene
1105
②
①
① .46 Moles per Liter
② .25
Hg 5461 A° EXCITATION

EXPLANATION OF PLATE VII

Excerpt from densitometer showing curves illustrating relative densities of 1650 cm^{-1} Raman line with concentrations.

PLATE VII

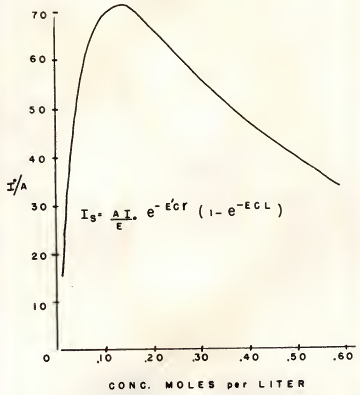
DENSITOMETER CURVES
RELATIVE INTENSITIES OF 1650 cm^{-1}
RAMAN LINE FOR C_8H_8

Hg 4358 Excitation

EXPLANATION OF PLATE VIII

Theoretical curve illustrating the theoretical relationship between concentration and intensity when the geometry of the system is considered and radiation is scattered from center of Raman tube.

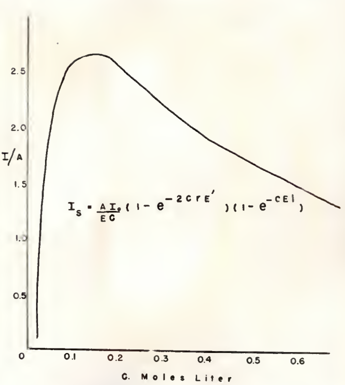
PLATE VIII


70
60
50
40
30
20
10
0
$I_\circ/A$
$I_S = \frac{A I_\circ}{E} e^{-E'cr} (1 - e^{-ECL})$
.10
.20
.30
.40
.50
.60
CONC. MOLES per LITER

EXPLANATION OF PLATE IX

Theoretical curve illustrating the theoretical relationship between concentration and intensity when the geometry of the system is considered and radiation is passing through the Raman tube normal to its surface.

PLATE IX


2.5
2.0
I/A
1.5
1.0
0.5
0
0.1
0.2
0.3
0.4
0.5
0.6
C. Moles Liter
$I_s = \frac{A I_0}{E C}(1 - e^{-2CrE'})(1 - e^{-CEl})$

EXPLANATION OF PLATE X

Theoretical curve illustrating the theoretical relationship between concentration and intensity when the geometry of the system is considered and when the average of the intensity of the radiation is passing through the Raman tube.

PLATE X

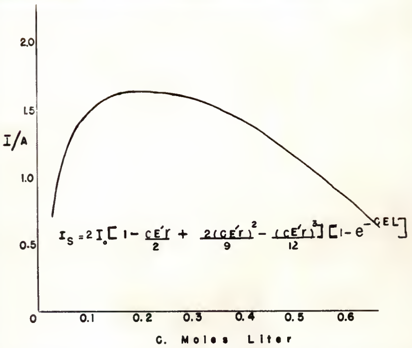

2.0
1.5
I/A
1.0
0.5
$I_S = 2 I_0 \left[1 - \frac{CE'r}{2} + \frac{2(CE'r)^2}{9} - \frac{(CE'r)^3}{12} \right] \left[1 - e^{-CEL} \right]$
0
0.1
0.2
0.3
0.4
0.5
0.6
C. Moles Liter

Table 1. Absorbency indexes for ferrocene.
(0.0499 gm. in 20 ml. $C_6 H_6$)

Wavelength	$\text{Log} \frac{I}{I_o}$	$\text{Log} \frac{I}{I_o}$	Molar Absorbency Index
400	.770	.768	57.462
410	.979	.980	73.059
420	1.130	1.120	83.582
430	1.210	1.220	91.044
440	1.240	1.250	93.283
450	1.240	1.240	92,537
460	1.190	1.190	88.805
470	1.075	1.075	80.223
480	.905	.904	67.462
490	.705	.703	52.462
500	.505	.507	37.686

Table 2. Absorption spectra of ferrocene

No.	Wavelength	$\log \frac{I}{I_o}$	Concentration moles/liter
1 (sample diluted 30 to 1)			
	400	0.860	0.448
	410	1.130	0.464
	420	1.210	0.434
	430	1.320	0.436
	440	1.350	0.434
	450	1.310	0.425
	460	1.240	0.422
	470	1.140	0.417
	480	0.945	0.421
	490	0.720	0.412
	500	0.494	0.396
		Average	0.428
2 (sample diluted 19 to 1)			
	400	0.89	0.294
	410	1.15	0.299
	420	1.30	0.297
	430	1.38	0.288
	440	1.41	0.287
	450	1.42	0.282
	460	1.32	0.283
	470	1.20	0.284
	480	1.01	0.285

Table 2 (cont.)

No.	Wavelength	$\text{Log}\frac{I}{I_o}$	Concentration moles/liter
	490	0.78	0.283
	500	0.54	0.273
		Average	0.286
3 (sample diluted 40 to 1)			
	400	0.800	0.558
	410	0.990	0.542
	420	1.150	0.551
	430	1.220	0.540
	440	1.250	0.535
	450	1.230	0.533
	460	1.170	0.526
	470	1.040	0.518
	480	0.870	0.518
	490	0.655	0.500
	500	0.461	0.495
		Average	0.528
4 (sample diluted 30 to 1)			
	400	0.841	0.429
	410	1.050	0.432
	420	1.200	0.431
	430	1.300	0.428
	440	1.330	0.428
	450	1.320	0.428

Table 2 (cont.)

No.	Wavelength	Log $\frac{I}{I_o}$	Concentration moles/liter
	460	1.250	0.422
	470	1.100	0.412
	480	0.920	0.409
	490	0.700	0.400
	500	0.490	0.389
		Average	0.419
6 (sample diluted 29 to 1)			
	400	0.710	0.368
	410	0.882	0.350
	420	1.020	0.354
	430	1.100	0.350
	440	1.130	0.352
	450	1.100	0.345
	460	1.050	0.344
	470	0.940	0.340
	480	0.775	0.334
	490	0.600	0.331
	500	0.422	0.326
		Average	0.326
7 (sample diluted 25 to 1)			
	400	0.570	0.247
	410	0.655	0.222
	420	0.815	0.242

Table 2 (cont.)

No.	Wavelength	$\log \frac{I}{I_o}$	Concentration moles/liter
	430	0.878	0.240
	440	0.890	0.237
	450	0.880	0.237
	460	0.838	0.235
	470	0.740	0.230
	480	0.610	0.226
	490	0.470	0.222
	500	0.315	0.207
		Average	0.222
8 (sample diluted 20 to 1)			
	400	0.550	0.191
	410	0.675	0.185
	420	0.780	0.187
	430	0.820	0.180
	440	0.860	0.184
	450	0.840	0.182
	460	0.800	0.180
	470	0.720	0.179
	480	0.595	0.177
	490	0.460	0.176
	500	0.315	0.168
		Average	0.189
11 (sample diluted 25 to 1)			
	400	0.650	0.283

Table 2 (cont.)

No.	Wavelength	$\log \frac{I}{I_o}$	Concentration moles/liter
	410	0.809	0.278
	420	0.935	0.280
	430	1.000	0.276
	440	1.040	0.280
	450	1.025	0.277
	460	0.990	0.279
	470	0.870	0.272
	480	0.725	0.269
	490	0.560	0.268
	500	0.398	0.266
		Average	0.285
12 (sample diluted 21 to 1)			
	400	0.640	0.234
	410	0.798	0.229
	420	0.919	0.231
	430	0.980	0.227
	440	1.010	0.228
	450	1.000	0.228
	460	0.940	0.222
	470	0.850	0.222
	480	0.710	0.221
	490	0.555	0.223
	500	0.392	0.219
		Average	0.225

Table 2 (cont.)

No.	Wavelength	Log $\frac{I}{I_o}$	Concentration moles/liter
13 (sample diluted 21 to 1)			
	400	0.352	0.127
	410	0.440	0.1265
	420	0.500	0.126
	430	0.540	0.125
	440	0.555	0.125
	450	0.549	0.1245
	460	0.520	0.123
	470	0.462	0.1205
	480	0.382	0.1190
	490	0.294	0.1185
	500	0.205	0.1150
		Average	0.123
14 (sample diluted 17 to 1)			
	400	0.345	0.102
	410	0.429	0.099
	420	0.490	0.099
	430	0.530	0.099
	440	0.540	0.0985
	450	0.535	0.0983
	460	0.510	0.098
	470	0.457	0.097

Table 2 (concl.)

No.	Wavelength	Log $\frac{I}{I_o}$	Concentration moles/liter
	480	0.380	0.096
	490	0.296	0.096
	500	0.206	0.0935
		Average	0.0977

Table 3. Ultraviolet absorption spectra of cyclooctatetraene.

No.	Wavelength	Log $\frac{I}{I_o}$	Concentration moles/liter
18-1 (sample diluted 401 to 1)			
	320	1.580	
	330	1.340 0.11*	4.80
	340	0.830	
	350	0.605	
18-2 (sample diluted 201 to 1)			
	320	2.00	
	330	1.55	2.72
	340	1.15	
	350	0.80	
	360	0.54	
	370	0.352	

Table 3 (cont.)

No.	Wavelength	$\log \frac{I}{I_0}$	Concentration moles/liter
18-3 (sample diluted 201 to 1)			
	320	1.68	
	330	1.22	2.13
	340	0.88	
	350	0.62	
	360	0.412	
	370	0.268	
18-4 (sample diluted 201 to 1)			
	310	1.68	
	320	1.20	
	330	0.850	1.48
	340	0.615	
	350	0.430	
	360	0.290	
	370	0.186	
18-5 (sample diluted 201 to 1)			
	310	1.40	
	320	0.990	
	330	0.710	1.24
	340	0.515	
	350	0.360	
	360	0.245	
	370	0.165	

Table 3 (cont.)

No.	Wavelength	$\text{Log}\frac{I}{I_o}$	Concentration moles/liter
18-6 (sample diluted 201 to 1)			
	300	1.41	
	310	1.00	
	320	0.69	
	330	0.494	0.865
	340	0.358	
	350	0.250	
	360	0.173	
	370	0.114	
18-7 (sample diluted 201 to 1)			
	300	1.14	
	310	0.785	
	320	0.540	
	330	0.385	0.674
	340	0.275	
	350	0.189	
	360	0.125	
	370	0.080	
18-8 (sample diluted 201 to 1)			
	300	0.818	
	310	0.560	
	320	0.395	
	330	0.284	0.455

Table 3 (concl.)

No.	Wavelength	$\log \frac{I}{I_o}$	Concentration moles/liter
	340	0.202	
	350	0.143	
	360	0.098	
	370	0.067	

*National Bureau of Standards

Table 4. Data for calibration curve.

Exposure	Log Exposure	Density
2400 sec	3.38021	.23147
1200 sec	3.07918	.16673
600 sec	2.77815	.10243
300 sec	2.47712	.04727
150 sec	2.17609	.01703
75 sec	1.87506	.00432

Table 5. Intensities of 1105 cm^{-1} Raman line.

Conc.	I_o	I	I_o/I	Log I_o/I	Log I	I/10
.084	19.7	19.4	1.015	.00647	.310	.48
.123	17.3	12.7	1.363	.13418	.76	.57
.181	15.4	10.7	1.440	.15836	.90	.80
.225	16.7	10.9	1.532	.18526	1.00	.10
.258	13.5	8.7	1.555	.19173	1.02	1.04
.285	15.4	11.8	1.305	.11561	.68	.48
.319	19.4	15.1	1.285	.10890	.62	.42
.465	17.3	15.6	1.110	.04532	.10	.12

Table 6. Intensities of 1650 cm^{-1} Raman line.

Conc.	I_o	I	I_o/I	Log I_o/I	Log I	I/100
.455	17.3	15.5	1.115	.04727	2.47	3.00
.674	12.7	10.5	1.210	.08279	2.70	5.01
.865	13.0	8.9	1.460	.16435	3.10	12.60
1.240	14.8	9.5	1.560	.19312	3.22	16.60
1.480	13.0	9.3	1.400	.14582	3.02	10.50
2.130	18.5	14.4	1.285	.10890	2.82	6.60
3.000	20.3	19.3	1.050	.02119	2.22	1.60

RAMAN SPECTRA OF CERTAIN COLORED SUBSTANCES AND THE EXISTENCE OF AN OPTIMUM CONCENTRATION FOR MAXIMUM INTENSITY OF SCATTERED RADIATION

by

ROBERT DWIGHT FISHER

B. S., Kansas State College
of Agriculture and Applied Science, 1953

AN ABSTRACT OF A THESIS

submitted in partial fulfullment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE

OF AGRICULTURE AND APPLIED SCIENCE

1954

A technique for obtaining Raman spectra of colored substances is described. Examples of Raman spectra of substances which partially absorb both the exciting and scattered radiation is given. Also, the disadvantages and advantages of using Hg 5461 A° and Hg 5770-90 A° lines for Raman excitation are compared with those for Hg 4047 A° and Hg 4358 A° lines.

The existence of an optimum concentration for obtaining the maximum intensity of scattered radiation for absorbing substances is illustrated with spectra of ferrocene and other compounds in suitable solvents.

Experimental curves giving the relative intensity of the 1105 cm^{-1} Raman line of ferrocene and the 1650 cm^{-1} Raman line of cyclooctatetraene as a function of concentration are shown. These are compared with three theoretical curves obtained from the consideration of the geometry of the system and the equation:

$$I_s = AI_o \left[1 - e^{-ckl} \right] / k$$

where k = extinction coefficient for scattered radiation

l = length of Ramam tube

c = concentration in moles/liter

I_o = incident intensity of exciting radiation

I_s = intensity of Raman radiation out of Raman tube

A = constant

It is pointed out that the theoretical considerations are inadequate, but that the discrepancy may be due to a concentration of electronically excited molecules in solution.

The technique demonstrated in this thesis will enable a person to obtain satisfactory Raman spectra of a number of colored compounds which previously have not been studied because it was thought that the Raman scattering would be completely absorbed.