AN INFRARED STUDY OF WATER IN SEVERAL INORGANIC CRYSTALLINE HYDRATES AND ORGANIC COMPOUNDS

by

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I. Introduction

This is a report on a study in which water in various substances was examined by utilizing infrared spectroscopic techniques. These substances variously ranged from several inorganic crystalline hydrates such as copper(II) sulfate pentahydrate, to several organic solvents such as acetone, and finally to two organic films derived from biological sources.

The study of water in any context requires that certain basic facts about water molecules be well in mind. The water molecule has three normal modes of vibration: a symmetrical stretching mode ν_1 , a bending mode ν_2 , and an antisymmetrical stretching mode ν_3 . The ν_1 mode may be visualized as two O-H groups oscillating in phase and the ν_3 mode may be visualized as two O-H groups oscillating out of phase. These three normal modes are illustrated here. The direction of the arrows shows the relative displacement of the nuclei and the lengths of the arrows show the relative amplitudes of the vibration. A change in dipole moment is associated with each of the modes, thus, each mode is infrared active.[1]
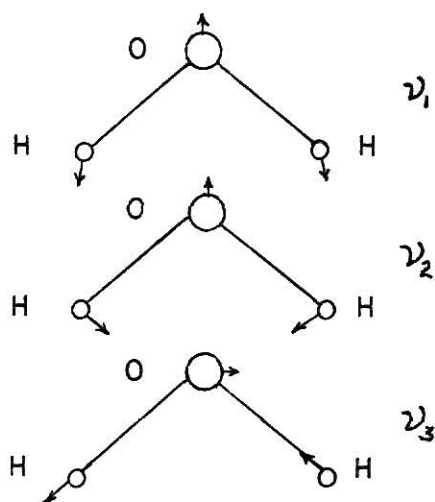
In the infrared spectrum of water vapor ν_1 and ν_3 are observed at 3657 and 3756 cm^{-1} respectively, while ν_2 is found at 1595 cm^{-1}. However, if the water molecule is bound to its

surroundings by hydrogen bonds, these observed frequencies are shifted. The fundamentals ν_1 and ν_3 are shifted to lower frequencies and ν_2 is shifted to higher frequencies. Furthermore, in strong interactions ν_3 is shifted a greater amount than ν_1 and the two absorption bands overlap.[2] Thus, for example, ν_1 and ν_3 are not separately observed in liquid water but the spectrum is characterized by a broad single band centered at about 3400 cm^{-1} resulting in part from this overlapping. Another component of this broad band is the overtone band $2\nu_2$. In this study we assumed that any water absorption band near 3400 cm^{-1} probably resulted from O-H stretching and that water bands in the vicinity of 1600 cm^{-1} probably resulted from the ν_2 vibration.

As a consequence of a water molecule being hydrogen bonded to its nearest neighbors in liquid water or ice, there are three modes of hindered rotation ν_L. Only one band arising from one of these modes is ordinarily observed in infrared absorption spectra. Also, as a result of the constraints imposed by hydrogen bonding to nearest neighbors there is a band attributed to hindered translation ν_T.

If we ignore losses caused by reflections at cell window interfaces an expression for the spectral transmittance $T(\nu)$ of a sample of thickness x may be written as

$$T = e^{-\alpha(\nu)x},$$

where $\alpha(\nu)$ is the Lambert absorption coefficient of the sample.

The imaginary part $n_i(\nu)$ of the index of refraction may be determined by the relationship

$$n_i(\nu) = \frac{\alpha(\nu)}{4\pi\nu}.$$

At a given temperature $\alpha(\nu)$ for an absorption band involving transitions between energy states m and n is directly proportional to $|R_{mn}|^2$ where R_{mn} is the matrix element connecting the two states. Since $n_i(\nu) = \alpha(\nu)/4\pi\nu$, $n_i(\nu)$ is also proportional to $|R_{mn}|^2$. The frequency at which $n_i(\nu)$ is a maximum must be considered the central frequency of a given absorption band. The central frequency of a broad band may be considerably different from the center of the observed band in the raw data.[3] For example, the absorption band arising from one of the ν_L modes is quite broad and centered at about 680 cm^{-1} in liquid water. However, $n_i(\nu)$ has been found experimentally to be a maximum at 570 cm^{-1}.[3] We therefore assign a frequency of 570 cm^{-1} for ν_L in liquid water. The ν_T band of liquid water is not nearly so broad as the ν_L band and the frequency of the center of the observed absorption band and the frequency at which $n_i(\nu)$ is a maximum nearly coincide at around 170 cm^{-1}.

It is well known that due to its geometry a water molecule is polar. Early workers found that simple electrostatic attraction of polar water molecules was not sufficient to explain the observed association of water molecules with one another and other types of polar molecules. In 1920, W.M. Latimer and W.H. Rodebush[4] proposed that the hydrogen atom of the water molecule is being shared by another oxygen atom. Actually, this "sharing" does not involve the proton but the electron of the hydrogen atom. The hydrogen electron that takes part in the O-H bond of the water molecule is shared with the oxygen atom of

another water molecule in the case of liquid water. The hydrogen atom stays principally associated with its original oxygen atom although the O-H bond length increases slightly. The energy of such a hydrogen bond is on the order of 5 Kcal per mole, which is 1/10 or 1/20 of the energy of a typical ionic or covalent chemical bond.[5] Thus, the hydrogen bond forms the middle ground between chemical bonds and the weaker, less specific van der Waals interactions which cause all known substances to liquify if the temperature is sufficiently low.[6]

As a starting point to gain experience in infrared spectroscopic techniques, we first examined simple inorganic crystalline hydrates. These crystals were chosen since their structures and infrared characteristics are well known and could serve as guides in the determination of the quality of spectra obtained and also could aid in learning to interpret infrared spectra.

The study of water in organic solvents was the next phase of investigation and represented a distinct increase in the complexity of the systems being examined. The complexity arises from both the polyatomic nature of organic substances and from the fact that liquids offer no regular structure for examination. Intermolecular interactions are complex, short lived, and of constantly varying strengths. There exists a continuum of interaction energies which results in some cases in broad, featureless absorption bands.

The final step in complexity was to examine water in two organic films derived from biological sources: agar, which is

a derivative of seaweed, and gelatin, which is derived from animal tissues. Agar is a carbohydrate and gelatin is a protein. Since water is the principal constituent of all biological systems, the study of its role in the structure of biological materials and, ultimately, its role in the life process is of great interest.

The study of biological materials and inorganic crystalline hydrates is, in large part, the study of the hydrogen bond. The structures of organic crystals and inorganic crystalline hydrates are determined by hydrogen bonds. Hydrogen bonds fix the structure of proteins. In fact, some feel that it is hardly an exaggeration to say that in the chemistry of living systems that the hydrogen bond is as important as the carbon-carbon bond.[6]

Finally, an unrelated study of the infrared spectral characteristics of glucose and certain high purity glucose polymers is presented as an appendix. This study was conducted in cooperation with Professor John Johnson of the Department of Grain Science and Industry, Kansas State University, who provided the samples.

II. Experimental Equipment and Procedures

A. Spectrometer

The data for this study were taken by means of a Perkin-Elmer Model 421 double beam grating spectrophotometer to scan the spectral region from 4000 to 550 cm^{-1}. Perkin-Elmer Corporation specifies that the instrument maintains a spectral slit width of less than 2.5 cm^{-1} at all times.[7] The calibration of the instrument was periodically checked throughout the period of data taking by using a polystyrene film reference. The calibration was maintained well within the manufacturer's specification of ± 1 cm^{-1}. Scan time to cover the entire spectral region was usually 25 minutes.

B. Hydrated Crystalline Salts

Two types of infrared windows were used in the study of the hydrated crystalline salts: calcium fluoride and silver chloride. Both types of windows were round, 25mm in diameter, and 5mm thick and were purchased from the Harshaw Chemical Company. Calcium fluoride windows are hard and have high transmittance in the spectral region from the visible to around 1500 cm^{-1}. Silver chloride windows are very soft but have good transmittance from the visible to around 500 cm^{-1}. Despite the wider transmittance range of silver chloride, the extreme softness of the material is a liability when one is working with gritty materials such as powdered crystalline salts. The windows rapidly become so scratched that they cannot be used. For

this reason silver chloride was used as a window material only in those spectral regions in which calcium fluoride could not be used; i.e., from 1500 to 550 cm^{-1}.

The hydrated salts used in this study were copper(II) sulfate pentahydrate, copper(II) chloride dihydrate, calcium sulfate dihydrate, and cobalt(II) chloride hexahydrate. All were analytical grade chemicals obtained from the Mallinckrodt Chemical Company. All but calcium sulfate were in large crystals which necessitated their being ground into a fine powder. This grinding was accomplished by using a "Wig-L-Bug" shaker, which is manufactured by the Crescent Dental Manufacturing Company, Chicago, Illinois. It has a cylindrical stainless steel capsule 23mm long and 13mm in diameter, which contains two 6mm ball bearings. This capsule holds the sample to be crushed. The cylinder with the sample and the two ball bearings enclosed was clamped to the end of an arm on the "Wig-L-Bug" and was shaken rapidly through a small arc. In effect, the shaker capsule and the ball bearings act as a tiny mortar and pestle. The length of time of shaking is govered by a built-in timer.

Microscopic examination of the powder resulting from 5 minutes' shaking revealed particles smaller than 8 microns in diameter, on the average. We discovered that if the powder were suspended in carbon tetrachloride and then allowed to settle for ten to fifteen seconds that the suppernatant liquid contained uniformly sized particles that could be recovered by decanting the supernatant and evaporating it under a hood. These particles were ideal for use in a mull.

A mull is a mixture of a finely divided sample in a liquid or semi-solid layered between two windows. The sample is suspended in the mulling material to reduce the reflection losses caused by abrupt changes of refractive index that would naturally occur as the sample beam of the spectrometer passes through the individual particles of a powdered sample. Two mulling materials were used: hexachloro 1,3 butadiene, obtained from the Eastman Chemical Company, and petroleum jelly of the brand called "Vaseline".

Ideally, the mulling material should not be absorbing in the spectral region of interest. For that reason butadiene was used in the spectral region 4000 to 2000 cm^{-1} and Vaseline was used in the spectral region 2000 to 550 cm^{-1}. Vaseline has a strong absorption band at 3000 cm^{-1} resulting from C-H stretching which would obscure part of the O-H stretching region of water, while butadiene does not absorb strongly at frequencies higher than 1600 cm^{-1}. Vaseline also has several absorption bands in the spectral region from 2000 to 550 cm^{-1} but they are sharp and easily recognized, whereas butadiene exhibits a multitude of bands which virtually obliterate much of this spectral region.

Butadiene is a colorless liquid of the consistency of water. Vaseline is a yellowish semi-solid. Use of two mulling materials which have two very different consistencies required two rather different techniques to get a thin film layered between two windows. When butadiene was the mulling material used, a small amount of powdered sample was placed in the center of one window which lay flat on a table. Two or three drops of butadiene from a

dropper were placed on this window, wetting the powder. The second window was then placed on top and rotated gently downward upon the bottom window until a thin, fairly uniform film of sample was distributed between the windows.

When Vaseline was used, the process was considerably easier. The sample was mixed with a small quantity of Vaseline in an agate mortar and pestle. A small amount of the mixture was placed on the very edge of one face of a window held in the hand. The second window was placed on top so that only one edge contacted the bottom window at the point where the mull was deposited. This formed a wedge-shaped space between the windows. The two windows were slowly pressed together so that the mull spread between the two faces of the windows into a thin, uniform film.

The two windows with the mull constitute a "cell". The cell was carefully clamped between two pieces of aluminum which had slot-shaped windows milled through them and were held tightly together with screws. This holder was then placed in the spectrometer sample beam. With the silver chloride windows it is necessary to use cardboard spacers to separate the silver chloride and the aluminum; left in direct contact with the aluminum the silver chloride would be reduced to elemental silver.

Due to the method of preparing the sample cell, no precise control could be exercised over the cell thickness or the concentration of the sample. This limitation prohibited obtaining any quantitative determination of absorption coefficients. The emphasis was only upon making the sample cell thin enough for fairly high transmittance in regions of non-absorption.

In order to assess the contribution of the water of hydration of the various salts it was necessary to heat the powdered samples in a ceramic crucible on a hotplate to remove the water of hydration for purposes of comparison of the spectra. We found that heating the sample for an hour at 250°C was more than sufficient in all cases to remove all water and to insure that the samples were anhydrous. The temperature of the sample was measured by placing one junction of a copper-constantin thermocouple into the sample, making sure that the junction was at least 5mm away from the wall of the crucible. The cold junction of the thermocouple was referenced in an ice water bath. Calibration for the thermocouple was obtained from the CRC Handbook of Chemistry and Physics.[8] This calibration was checked with boiling water and ice water against a laboratory mercury thermometer. The results agreed to within ±1°C. Thermocouple voltages were measured with a Honeywell Model 2702 potentiometer.

When heated at 250°C for only a few minutes, hydrated copper sulfate changes from a rich blue to a greyish white. This color change represents a transition from the pentahydrous to the anhydrous state. Cobalt chloride has two distinct hydrated states. Before heating, the crystals are in the reddish purple hexahydrous state. When heated, the crystals turn first into a deep purple, which corresponds to the dihydrous state. Further heating ultimately yields the royal blue anhydrous form. Copper chloride dihydrate is turquoise before heating and brown in the anhydrous state. Calcium sulfate is white in both the

dihydrous and anhydrous states.

All of the anhydrous forms of the salts are extremely
hygroscopic; thus, making a mull without contamination by at-
mospheric humidity was difficult. Speed was the only solution
when making a mull with butadiene. Making a mull with Vaseline
was easier if the mortar and pestle were heated and a bit of
Vaseline were melted in the bottom of the mortar. The anhydrous
sample could be added to the melted Vaseline directly from the
heating crucible. The melted Vaseline immediately covered the
sample, protecting it from atmospheric humidity. The critereon
for whether or not the sample was completely anhydrous was the
presence or absence of the strong 3400 and 1600 cm^{-1} water bands
in the spectrum. Both of these bands appeared when only minute
traces of water were present. Absence of these bands was con-
sidered proof of the anhydrous state.

Copper sulfate pentahydrate was selected for further de-
tailed examination of the process whereby the hydrated crystal
gives up its waters of hydration. The samples were powdered
as usual and were heated for 90 minutes in a crucible at tem-
peratures that ranged from 30° to 132°C in 10-15 Cdeg increments
on a hot plate. The various temperatures on the hot plate were
obtained by use of a variable transformer to control the voltage
supplied to the hot plate. Temperatures were monitored by the
thermocouple technique previously described. A fresh sample
was used for each temperature increment.

C. Organic Solvents

For the study of organic solvents round windows 25mm in diameter and 5mm thick made of KRS-5 (thallium bromoiodide) obtained from the Harshaw Chemical Company were used for the cells. This type of window was selected because of its superior transmittance over a wider spectral range than silver chloride and because the polished windows are noticeably flatter than silver chloride. For the making of liquid cells it is necessary to have windows that are as flat as possible so that the edges of the cell may be readily sealed.

Since the three organic solvents examined, acetone, acetonitrile, and methanol, are all volatile liquids it was not sufficient to merely trap a thin layer of liquid between two cell windows. In order to insure that the samples did not evaporate and also to insure that the liquid cells be of controllable and reproducible thickness, spacers of polyethylene were prepared to place between the windows. Several thicknesses of polyethylene were used, ranging in thickness from 10 to 70 microns. Annular rings the diameter of the windows were cut with a razor blade and were coated with a thin film of General Electric electrical insulating compound--a silicone grease--so that the edges of the cell would seal. This grease was selected because it showed negligible solubility in the solvents used. Nevertheless, we exercised care to insure that there was only minimal contact between the solvent and the grease.

All of the solvents were first tested to determine the thickness of the cell necessary to exhibit good absorption bands

without being excessively opaque. We found that a 70 micron spacer was satisfactory for acetonitrile and acetone. Methanol proved to be as strong an absorber as liquid water, and the best results were obtained with no spacer at all. The problem of evaporation was solved by applying silicone grease with a small brush to the edges of the windows after they had been clamped in the holder. Without a spacer between the windows the thickness of the liquid film trapped between the faces was a function of how tightly the cell was clamped in the holder. This uncertainty made working with methanol difficult. The cell thickness was certainly less than 10 microns and was probably closer to 5 microns.

We next examined the effect on the spectrum of each solvent of small amounts of water added as a contaminant. Starting with the pure solvent and progressing through increasing amounts of water contamination, we recorded a series of spectra. All quantities of solvent were carefully mixed immediately prior to use so that atmospheric water not be absorbed by the sample. We arbitrarily terminated the water contamination series of each solvent when the region of the spectrum below 1500 cm^{-1} became almost opaque due to the intense water absorption.

D. Organic Films

Two organic films were selected for study. The first of these films, agar, was made from Difco Bacto-Agar made by Difco Laboratories. Agar is a common growth medium for bacteria cultures. It is supplied in a dry, granular form and is prepared

by dissolving 2g of agar in 100g of water and by heating this solution at 120°C in an autoclave for about five minutes. Immediately upon removal from the autoclave the agar solution is a slightly viscous straw-colored liquid. The solution was poured onto clean glass plates so that it formed a relatively uniform 1-2mm thick sheet.

After the liquid agar cooled below 50°C it solidified into a clear, firm and gelatinous sheet and could be easily removed from the glass plate by slipping a small spatula between the sheet and the glass and by slowly lifting the sheet away from the glass.

Left exposed to the air, the sheet slowly dries into a thin, transparent film. The film will dry to the point where the water in the film comes into equilibrium with the water vapor in the air. A 1mm thick wet film would air dry to a transparent, wrinkled film about 30 microns in thickness in 24 hours. Since the humidity in the laboratory was rarely less than 50 per cent, the air dried films still had significant amounts of water.

The drying of the agar film could be considerably speeded up by drying it under vacuum. The freshly solidified wet film was placed between two pieces of stainless steel screen in the bottom of a bell jar. A small brass weight was placed on top of the screen. Use of the screen allowed rapid drying from both sides of the film and the weight made the film dry flat. A small vacuum pump pumped on the bell jar during the entire drying process. However, we found that the vacuum drying caused the water in the film to slowly freeze, which resulted in a film

that was cloudy when it dried. This difficulty was solved by gently heating the bell jar on a hot plate while the jar was being pumped. Films dried under vacuum could be produced in two or three hours. In addition to saving time, the films dried in this manner were quite dry rather than just in equilibrium with the water vapor in the air, as were the air dried films.

By weighing the wet film on a microgram balance immediately after solidification it was possible to calculate what the weight of the dry film should be. By a subsequent weighing of the film at any stage of drying we could calculate the percentage weight of the water in the film at a given time. However, due to the marked tendency of the film to equilibrate with atmospheric humidity, its weight would measureably change during the weighing process itself. Thus, all weighing was done as quickly as possible. The dried film is also extremely hygroscopic. This unfortunately meant that a film supposedly dry at the start of a scan on the spectrometer had absorbed water by the time the end of the scan was reached. To minimize this problem scans were limited to only those spectral regions of interest and were made as quickly as possible. The spectral region of interest in the agar was from 2500 to 1800 cm^{-1}.

A typical run would start with a thoroughly dry film that had been weighed prior to drying in order to calculate the dry weight. The dry spectrum was then recorded. Immediately after the first run we would again quickly weigh the film and then record the spectrum again. After each weighing the percentage weight of water in the film would be calculated. This procedure

continued as long as the film continued to absorb moisture from the air. The most dramatic changes occurred in the first ten minutes after removal of the film from the vacuum drying jar. These changes progressively slowed as time passed.

We next examined the effect of the various potassium halides, KF, KCl, KBr, and KI, upon the associational band ν_α of water in the agar film. We found that the adding of 2g of the halide salt to 100g of hot agar solution made a satisfactory film. Any more halide salt than this caused the film to dry cloudy or prevented it from solidifying at all.

The agar solution with the added halide salt was made into a film and dried under vacuum as previously described. The dried film was placed in the spectrometer and monitored by continuous running of the spectrum between 2500 and 1800 cm^{-1} until the film had absorbed enough moisture from the air to develop a sufficiently strong associational band to determine its location accurately. This procedure was repeated for agar films with each of the four potassium halides.

We then considered films made from gelatin. For this study we used Knox's Unflavored Gelatin. After a few tries we found that a sufficiently tough film could be made by mixing 2g of gelatin and 15g of water and then by gently heating the mixture until the gelatin dissolved. A slightly viscous liquid results. As before when we were making agar films, we poured the liquid onto glass plates, allowed it to cool, removed the film from the glass, and then dried it under vacuum in a bell jar. The resulting clear and colorless film was tough and rigid. Typically, a 2mm

thick wet film would dry to a thickness of about 0.2mm. The dried film could then be easily clamped into a sample holder and placed in the spectrometer.

Gelatin showed little inclination to surrender all of its water even after lengthy drying periods. It also showed little inclination to absorb significant amounts of water from the air. As a consequence, a series of spectra with varying amounts of water was not taken.

The film could have been examined as it dried on a sample holder. However, as the film dries it adheres tightly to whatever it touches. Thus, although it would have been possible to record the spectrum of the drying film, it would not have been possible to weigh the film to determine its water content. A scale sensitive enough to weigh the changes in weight of the film as it lost water could not stand the weight of the aluminum holder and sample.

We next took a series of spectra of gelatin films with potassium halides added, as we did with agar. A satisfactory film that would gel was made with 1.8g of gelatin, 0.5g halide salt, and 15g of water. However, these films turned opaque in both the visible and infrared after drying. This probably resulted from from the salts crystalizing out. The tiny salt crystals probably caused significant light scattering, which resulted in the film appearing opaque. A freshly gelled film of gelatin that contained a halide salt was draped across the aperture of a sample holder and allowed to air dry. Just before the film became dry enough for the halide salt to start crystallizing out, we

recorded the spectrum as quickly as possible. Usually the heat
of the sample beam was sufficient to complete the drying of the
film on the part of the film where the image of the source was
focused and the film rapidly became opaque. Thus, that particular
film was of no further use. By using this technique we recorded
the spectra of gelatin with the four potassium halide salts.

III. Results and Discussion

A. Hydrated Crystalline Salts

1. Copper Sulfate

The spectra of hydrous and anhydrous copper sulfate are
shown in Figure 1. The spectrum of the anhydrous sample (trace
2) is discontinuous at 2000 cm^{-1}. This is the frequency where
the cell was changed from a butadiene mull with calcium fluoride
windows to a Vaseline mull with silver chloride windows. The
spectrum of the hydrated sample (trace 1) happens to exhibit no
discontinuity. The hydrated samples in later figures show ob-
vious discontinuities. A spectral region having no significant
absorption bands was purposely selected for the changeover point
for the two mulls because of the expectation that the traces re-
sulting from the use of two mulls and window materials would not,
except by chance, coincide.

The most obvious changes from the hydrous to the anhydrous
states that we see in Figure 1 are the disappearance of the broad
absorption band centered at 3350 cm^{-1} and the narrower band at
1650 cm^{-1}. These bands in the hydrate spectrum are obviously

Figure 1. Curve 1: Spectrum of copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). Curve 2: Anhydrous copper(II) sulfate. The "v"'s in the figure indicate uncompensated Vaseline absorpton bands.

CuSO₄
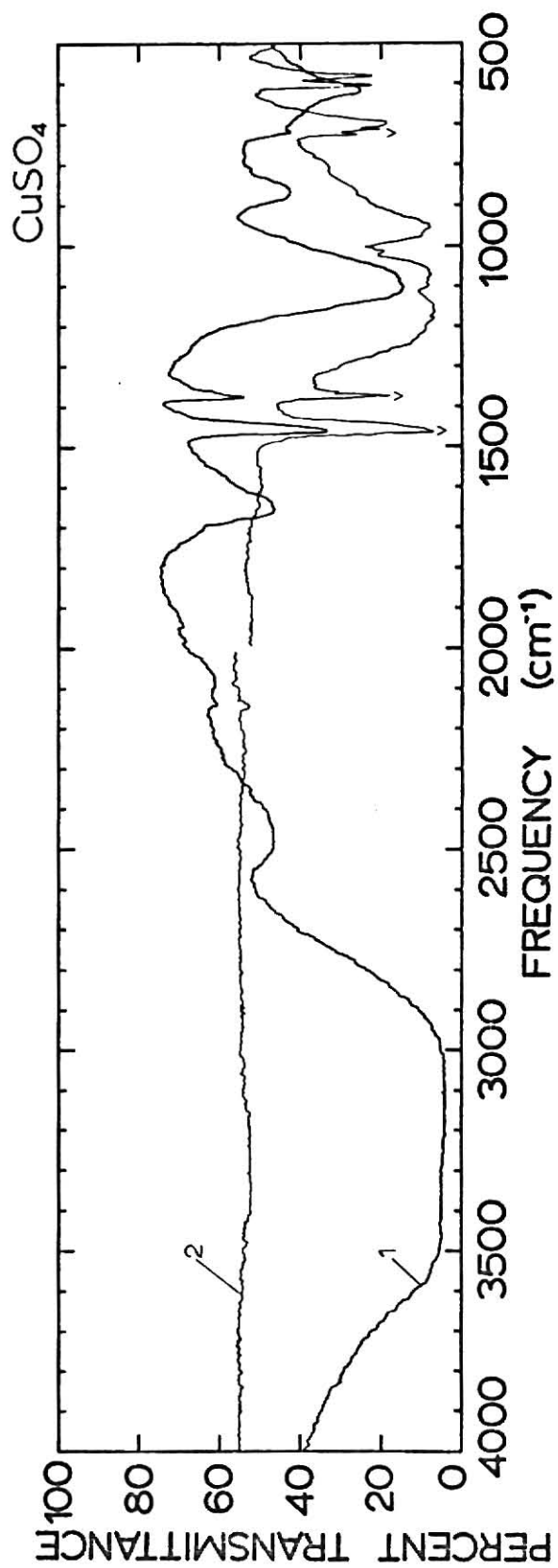
due to the presence of water. The 3350 cm^{-1} band corresponds to the broad O-H stretching band of liquid water, which is found at about 3400 cm^{-1} in pure water. The copper sulfate 1650 cm^{-1} water band corresponds to the 1620 cm^{-1} ν_2 band in liquid water.

The weak bands at 2460 and 2090 cm^{-1} in the hydrate spectrum are also missing in the anhydrous spectrum. One or both of these bands are probably associational or overtone bands.

At 1460, 1375, 1360, 730, and 720 cm^{-1} are sharp bands common to both the hydrous and anhydrous spectra. These bands arise from the Vaseline used in the mull. For ease of identification, the Vaseline bands in Figures 1-4 have been labelled with a "V".

There are several obvious differences between the hydrous and anhydrous spectra at frequencies lower than 1000 cm^{-1}. Most interesting is the change from a sharp and well defined absorption band at 610 cm^{-1} in the hydrous spectrum to a pair of sharp bands at 600 and 580 cm^{-1} in the anhydrous spectrum. The 610 cm^{-1} band in the hydrous spectrum probably corresponds to the liquid water ν_L band which has a transmittance minimum at 680 cm^{-1}. The sharp pair of bands in the anhydrous spectrum probably result from sulfate absorption bands that we obscured by the water band in the hydrate.

Figure 2 shows the effects of heating at various temperatures for 90 minutes upon the broad 3300 cm^{-1} O-H stretching band of copper sulfate pentahydrate. Curve 1 is the hydrate prepared with no heating, while curve 2 resulted from the sample being heated at only 30°C. By comparing curves 1 and 2 one gets an indication of the presence of two broad bands in curve 1 at

Figure 2. Copper(II) sulfate pentahydrate heated for 90 minutes at (1) room temperature (24°C), (2) 30°C, (3) 50°C, (4) 58°C, (5) 67°C, (6) 77°C, (7) 95°C, (8) 110°C, (9) 122°C, (10) 132°C.

CuSO₄
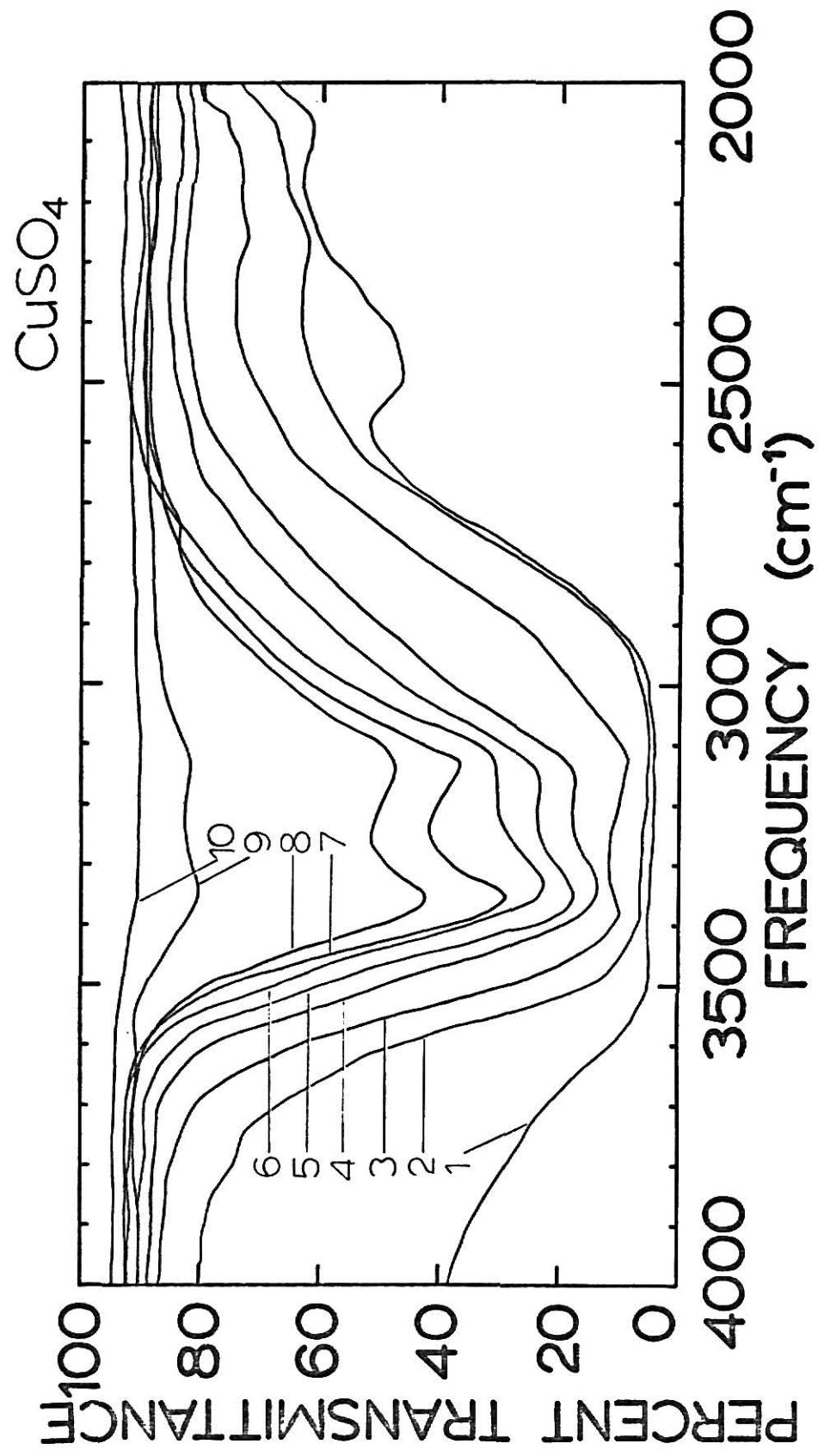
around 3500 and 3000 cm^{-1} that are greatly diminished in curve 2. The presence of these bands at room temperature would help to explain the wide shoulders on the 3300 cm^{-1} band. Apparently, gentle heating is sufficient to remove significant amounts of the water responsible for these broad shoulders. Further heating results in the band narrowing somewhat and also separating into two new bands at 3355 and 3140 cm^{-1}. Finally, after the sample has been heated at 132°C for 90 minutes, all of the water appears to have left the crystal, since curve 10 is essentially flat.

Of interest is the fact that after gentle heating of the sample the two bands at around 2460 and 2090 cm^{-1} which are present in curve 1 of Figure 2 disappear and are replaced by a very weak single band at around 2250 cm^{-1}. This band also disappears after the sample has been heated at 58°C for 90 minutes (curve 4).

Seidl, et al.[9] discuss the effect of waters of hydration in crystallographically nonequivalent sites. If n is the number of molecules at nonequivalent sites, there are 2n stretching fundamentals ν_1 and ν_3 and n bending fundamentals ν_2 of the water molecule. Actual determination of the number n by using infrared spectroscopy requires substitution studies utilizing HDO and D_2O. The present study did not include this technique. However, the structure of copper sulfate and, in particular, the location of the water molecules in the crystal have been determined by electron and x-ray diffraction for all of the atoms except the water hydrogens. The hydrogen atoms have been located by using neutron diffraction.[10] Four of the five water molecules are tetrahedrally placed about the copper atom, while the fifth water

molecule is adjacent to two sulfate oxygen atoms and to two of the other water molecules. Thus, we see that there are two non-equivalent sets of water molecules; i.e., n=2. The observation of four O-H stretching bands during the dehydration series of copper sulfate is consistent with this value of n. We recall that absorption bands at 3355 and 3140 cm^{-1} were discovered when the sample had been heated slightly. For n=2 there should also be two bending fundamentals. If there are two bands, the present study did not resolve them.

The origin of the two bands in Figure 2 seen in the unheated sample spectrum at 2460 and 2090 cm^{-1} is not fully understood. The fact that there are two bands seems to be related to the fact that there are two sites for water in the crystal. The two bands are in the wrong location and too far appart to be simply explained as associational bands arising from a split ν_2 band.

We had first thought that one or both of these bands may be the result of water adsorbed onto the surface of the crystal. If this were so, we reasoned, these bands should be made more intense if the crystals were exposed to high humidity for a length of time. A powdered sample was placed in a chamber at 100 percent relative humidity for 36 hours. The spectrum of this sample showed no change in the intensity of these bands. The same sample was pumped under vacuum for over 24 hours in an attempt to remove any adsorbed water. Again, no change in these two bands was observed in the spectrum.

The single band at 2250 cm^{-1} that remains after gentle heating is probably a ν_a band since it can be obtained from the combination

$$\mathcal{V}_2 + \mathcal{V}_L = 1650 \text{ cm}^{-1} + 610 \text{ cm}^{-1} = 2260 \text{ cm}^{-1}.$$

In the CRC Handbook of Chemistry and Physics[11] we see that copper sulfate loses four of its five waters of hydration at 110°C and loses the fifth molecule at 150°C. We see in Figure 2 that it was obviously not necessary to use temperatures this high to remove significant amounts of the water. This apparently contradictory result is somewhat puzzling. The temperatures were measured by a thermocouple purposely kept away from the wall of the heating crucible. At the higher temperatures that were used the temperature at the wall of the crucible was probably much higher than the temperature the thermocouple measured. But this does not explain the dramatic change in the spectrum after heating the sample to the very modest temperature of 30°C.

It is possible that the waters of hydration may be removed at low temperatures by heating for long periods of time. The water molecules of the crystal probably have a Boltzman distribution of energies. A small but finite number of molecules possess sufficient energy to leave the crystal. As soon as they leave, more energy is added to the system by the hotplate and the energy of the system redistributes itself. In this manner much of the water could be driven off.

The fact that the four water molecules associated with the copper atom leave the crystal at lower temperatures than the fifth water molecule suggests that the bands at 3500 and 3000 cm^{-1} which disappeared after gentle heating of the crystal were caused by the four molecules around the copper atom. If this is

Figure 3. Curve 1: Spectrum of copper(II) chloride dihydrate (CuCl$_2$.2H$_2$O). Curve 2: Anhydrous copper(II) chloride.
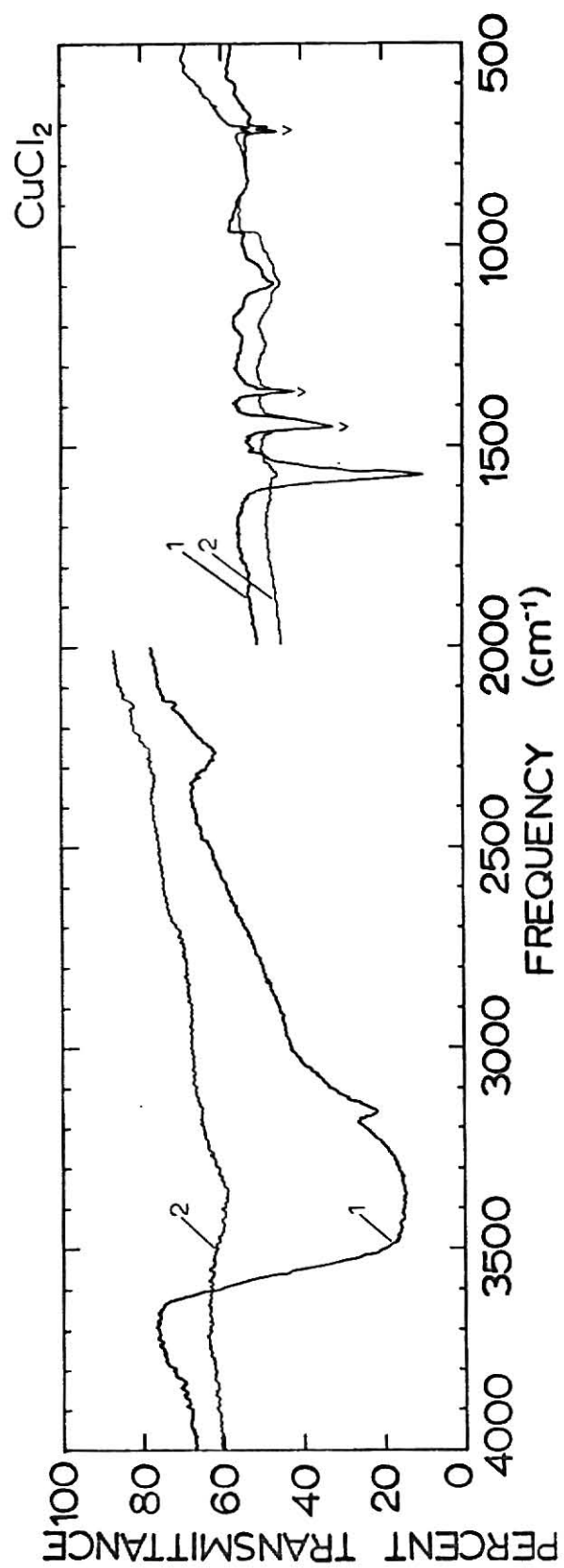
so, the two bands at 3355 and 3140 cm^{-1} that persisted until relatively high temperatures were reached, may result from the fifth water molecule. The disappearance of the two unexplained bands at 2460 and 2090 cm^{-1} after slight heating suggests that they, too, are associated with the four water molecules around the copper atom. The weak 2250 cm^{-1} band that is visible after the 2460 and 2090 cm^{-1} bands disappear seems consistent with the intensity of an absorption band arising from a single water molecule per unit cell.

2. Copper Chloride

The most obvious differences between the hydrous and anhydrous spectra of copper chloride shown in Figure 3 lie in the broad 3400 cm^{-1} band and the 1580 cm^{-1} band. The bands are absent in the anhydrous copper chloride spectrum. A weak but sharp band appears at 3165 cm^{-1} on the low frequency side of the 3400 cm^{-1} band. The 1580 cm^{-1} band is probably the ν_2 band and the 3165 cm^{-1} band may be the overtone $2\nu_2$.

In the hydrous spectrum is a single absorption band at 2270 cm^{-1} which is probably the ν_a band. Since ν_2 is at 1580 cm^{-1} one would expect to observe a ν_L band at 690 cm^{-1}; however, no band at all is observed near this frequency. It may be that the ν_L band that is usually seen at about this frequency is not infrared active in this case due to the particular environment of the water molecules in copper chloride.

Wyckoff[12] lists copper chloride dihydrate as having the copper atoms surrounded by two chloride ions and two water

Figure 4. Curve 1: Spectrum of cobalt(II) chloride
hexahydrate ($CoCl_2 \cdot 6H_2O$). Curve 2: Anhydrous
cobalt(II) chloride.
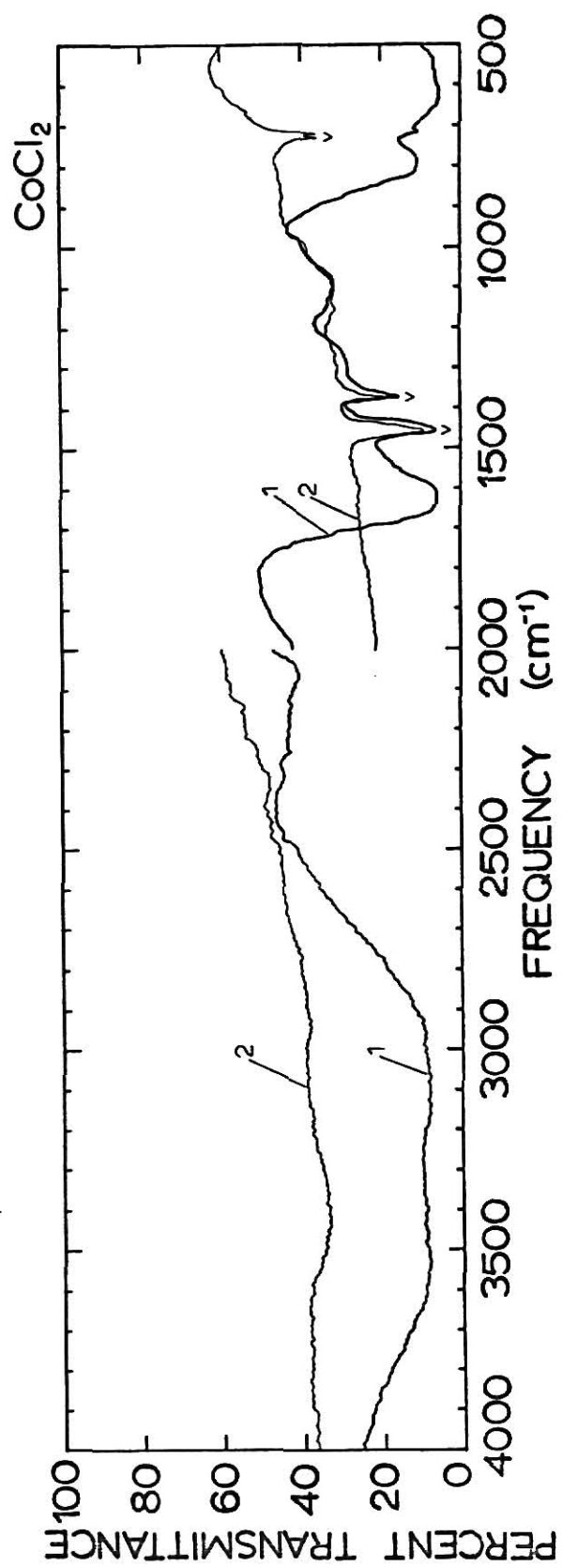
molecules. Thus, the water molecules are in equivalent sites and give only two stretching fundamentals and one bending fundamental. Since only one broad band was observed in the O-H stretching region around 3400 cm^{-1} we assume that the two stretching fundamentals overlap as in liquid water. As a consequence of the single bending frequency, the ν_2 band at 1580 cm^{-1} is unusually sharp when compared with the other hydrates studied.

3. Cobalt Chloride

In figure 4 cobalt chloride hexahydrate shows a very broad band centered at about 3300 cm^{-1}. The band shows indications of being composed of two broad bands located at about 3600 and 3100 cm^{-1}. These bands are not obvious in the photographically reduced spectrum in Figure 4. The original spectrum shows them more clearly. These two bands overlap to form the unusually broad band centered at 3300 cm^{-1}.

The water ν_α band is located in the general vicinity of 2100 cm^{-1}. This band is quite broad in cobalt chloride hexahydrate compared to the other hydrates and it is difficult to locate its center accurately. The ν_2 band is at 1625 cm^{-1} and is also relatively broad.

Cobalt chloride hexahydrate has four water molecules around the cobalt atom at the corners of a distorted square and two other water molecules unrelated to this grouping are associated between the chloride ions and the other water molecules.[13] Thus, there are two nonequivalent sets of water molecules. This interpretation is supported by the presence of the two bands

comprising the very wide O-H stretching band shown in Figure 4. Also, the unusual width of the ν_2 band suggests that it may result from an unresolved pair of absorption bands.

Comparison of the spectra of the hydrous and anhydrous salts shows water bands at 800 and 600 cm^{-1}. The 600 cm^{-1} band is likely a ν_L band. We mentioned earlier that there are, in fact, three ν_L bands and that two of these bands are not normally infrared active. One of the bands in liquid water not normally observed with infrared spectroscopy is found at around 760 cm^{-1} with Raman spectroscopy. It may be possible that the environment of the water molecules is such that the band that we observed at around 800 cm^{-1} results from a ν_L mode now made infrared active.

4. Calcium Sulfate

Calcium sulfate dihydrate has a structure in which $CaSO_4$ layers are spearated by sheets of water molecules.[14] Since all of the water molecules are in crystallographically equivalent sites we would expect that the ν_2 band would be a single, relatively sharp band as with copper chloride. This is not, in fact, what is observed.

The O-H stretching band in the calcium sulfate dihydrate sample shows indications of being composed of two overlapping absorption bands. This observation is perhaps not obvious in the reduced scale of Figure 5, but it is apparent in the original spectrum. These bands are centered at about 3350 and 3400 cm^{-1}.

Figure 5. Curve 1: Spectrum of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). Curve 2: Anhydrous calcium sulfate.
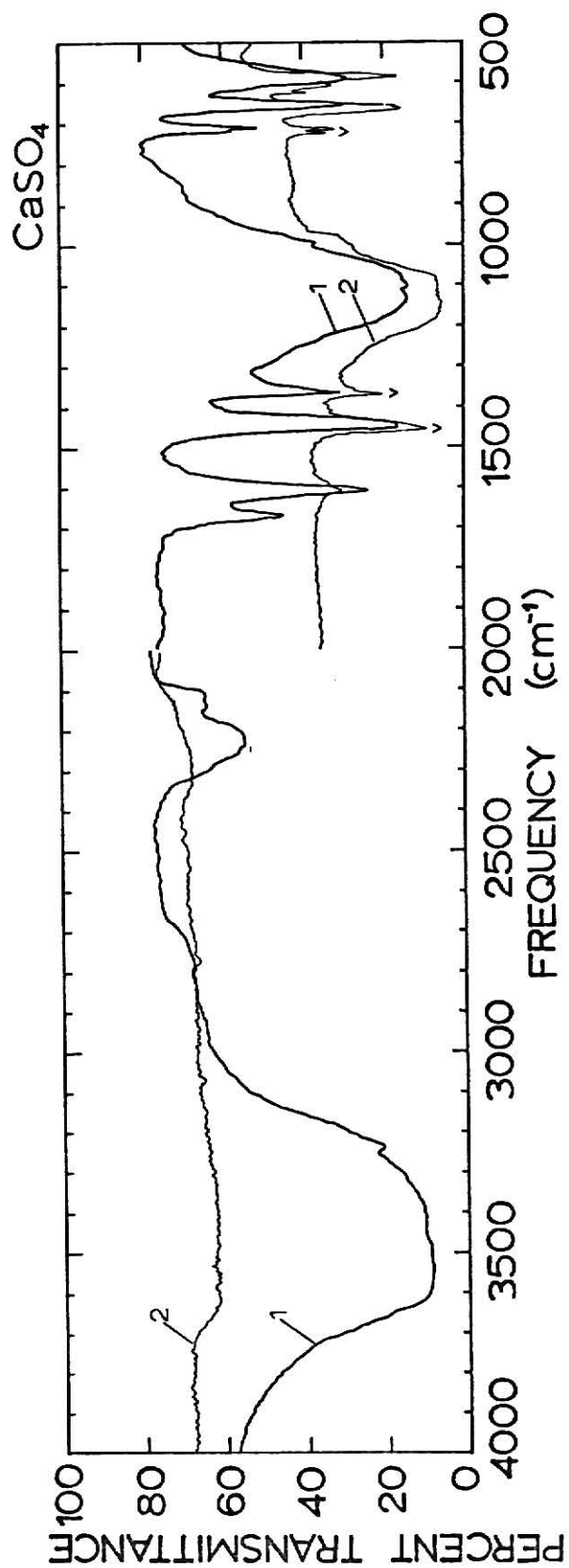
The location of these two bands is in good agreement with Seidl, et al.[9] who found distinct bands at 3549 and 3404 cm^{-1} in the spectrum of a crystal of gypsum ($CaSO_4 \cdot 2H_2O$). Another very weak but reproducible band is located on the low frequency shoulder of the 3400 cm^{-1} band at about 3235 cm^{-1}.

The water ν_α band is apparently composed of several over-lapping bands of varying intensity. The most intense band is at 2230 cm^{-1} and a pair of weak bands are at 2140 and 2110 cm^{-1}. The water ν_2 band is also split. There is a band at 1685 cm^{-1} and another of greater intensity at 1610 cm^{-1}.

Since we observe doubling of the ν_2 band despite the supposed equivalency of the water molecules, we conclude that these bands arise as a consequence of two coupled vibrations of the water molecules present in the unit cell. The presence of two isolated O-H stretching bands may indicate that there are two distinct OH groups in the crystal.[9] It is possible that the water molecules occupy equivalent sites but are distorted; i.e., the O-H bonds of a given molecule are of different lengths.

As a result of coupling of the water molecules in the unit cell Hass and Sutherland[15] maintain that four ν_2 bands are to be expected. In fact, bands at 1660 cm^{-1} [16] and 1632 cm^{-1} [17] have been reported in gypsum in addition to the two previously men-tioned bands and were assigned to ν_2 by Hass and Sutherland. These two extra bands were not observed in this study.

Comparison of the 590 cm^{-1} band present in both the hydrous and the anhydrous spectra of Figure 5 shows a shoulder on the low frequency side of this band in the hydrous spectrum which

appears to be caused by a weak band located at about 570 cm^{-1}. The strong 590 cm^{-1} band present in both spectra is due to the sulfate ion.

Hass and Sutherland report bands at 580 and 450 cm^{-1} which they associate with ν_L. The value of 580 cm^{-1} agrees well with the location of the weak water band that we estimated to be at 570 cm^{-1}.

If the existence of four ν_2 bands is granted, one can then explain some of the general features of the complex ν_a band centered at about 2200 cm^{-1} in Figure 5. This complex of bands contains a relatively strong band at 2230 cm^{-1} which is asymmetrical enough to suggest that it may consist of several unresolved weaker bands. On the low frequency shoulder of this band are two weak, closely spaced bands at 2110 and 2140 cm^{-1}. Combinations of the four frequencies of ν_2 and the two frequencies of ν_L yield eight associational bands $\nu_2 + \nu_L$. Three of these bands are at 2230, 2135 and 2110 cm^{-1}. These frequencies are in good agreement with the frequencies of the bands that were resolved.

5. Summary of the Hydrated Salts Results

The suggested assignments for the various water bands observed in the hydrated salts are summarized in Table 1. We were not successful in finding plausible explanations for the origins of two bands in copper sulfate and some of the other band assignments are, admittedly, speculative.

Nevertheless, it is clear that our choice of hydrated salts was fortuitous. Each of the salts demonstrated the effect of

Table 1. The location of the observed water bands in the hydrated crystals and their suggested assignments.

Hydrate	Band (cm^{-1})	Suggested Assignment
$CuSO_4 \cdot 5H_2O$	3500	ν_3 *
	3350	ν_3 **
	3140	ν_1 **
	3000	ν_1 *
	2460	?
	2250	$\nu_2 + \nu_L$
	2090	?
	1650	ν_2
	610	ν_L
$CuCl_2 \cdot 2H_2O$	3400	ν_1, ν_3
	3165	$2\nu_2$
	2270	$\nu_2 + \nu_L$
	1580	ν_2
	690$^+$(est.)	ν_L
$CoCl_2 \cdot 6H_2O$	3600	ν_1, ν_3 *
	3300	ν_1, ν_3 **
	2100	$\nu_2 + \nu_L$
	1625	ν_2
	800	ν_L
	600	ν_L
$CaSO_4 \cdot 2H_2O$	3350	ν_1, ν_3 *
	3400	ν_1, ν_3 **
	3235	$2\nu_2$
	2230	$\nu_2(2) + \nu_L(1)$
	2140	$\nu_2(1) + \nu_L(2)$
	2110	$\nu_2(2) + \nu_L(2)$
	1685	$\nu_2(1)$
	1660$^+$	$\nu_2(2)$
	1632$^+$	$\nu_2(3)$
	1610	$\nu_2(4)$
	570	$\nu_L(1)$
	450$^+$	$\nu_L(2)$

* Water site #1
** Water site #2
+ Not observed

a water molecule's placement in a crystal lattice upon the infrared absorption spectrum of that salt. Three different distributions of waters of hydration were illustrated by the samples studied.

Copper chloride proved to be the simplest crystal studied. Its two waters of hydration were located in identical sites. This symmetrical placement of the water molecules resulted in a single broad O-H stretching band and a single, relatively sharp ν_2 band.

Both copper sulfate and cobalt chloride had two distinct species of water molecules in their crystal structures. We saw how the presence of nonequivalent sites for water molecules resulted in the formation of two distinct O-H stretching bands and a broad ν_2 band that may result from two overlapping ν_2 bands.

Calcium sulfate was the most interesting of the salts, in some respects. Although the water molecules in the crystal are in equivalent sites, they are distorted into asymmetrical configurations. This distortion of the water molecules and coupling of the vibrations of the water molecules in the unit cell resulted in a complex of water bands that included a very broad double O-H stretching band and a pair of ν_2 bands.

B. Organic Solvents

1. Acetone

The spectrum of pure acetone is shown in Figure 6, curve 1. The spectrum is characterized by intense absorption bands in almost all frequency regions of the spectrum. Curves 2-9 of Figure

Figure 6. Curve 1: Pure acetone. The remaining curves are acetone containing increasing amounts of water, measured by volume: (2) 0.7%, (3) 1.5%, (4) 2%, (5) 4%, (6) 8%, (7) 12%, (8) 26%, (9) 41%.

ACETONE

PERCENT TRANSMITTANCE

FREQUENCY (cm⁻¹)

41
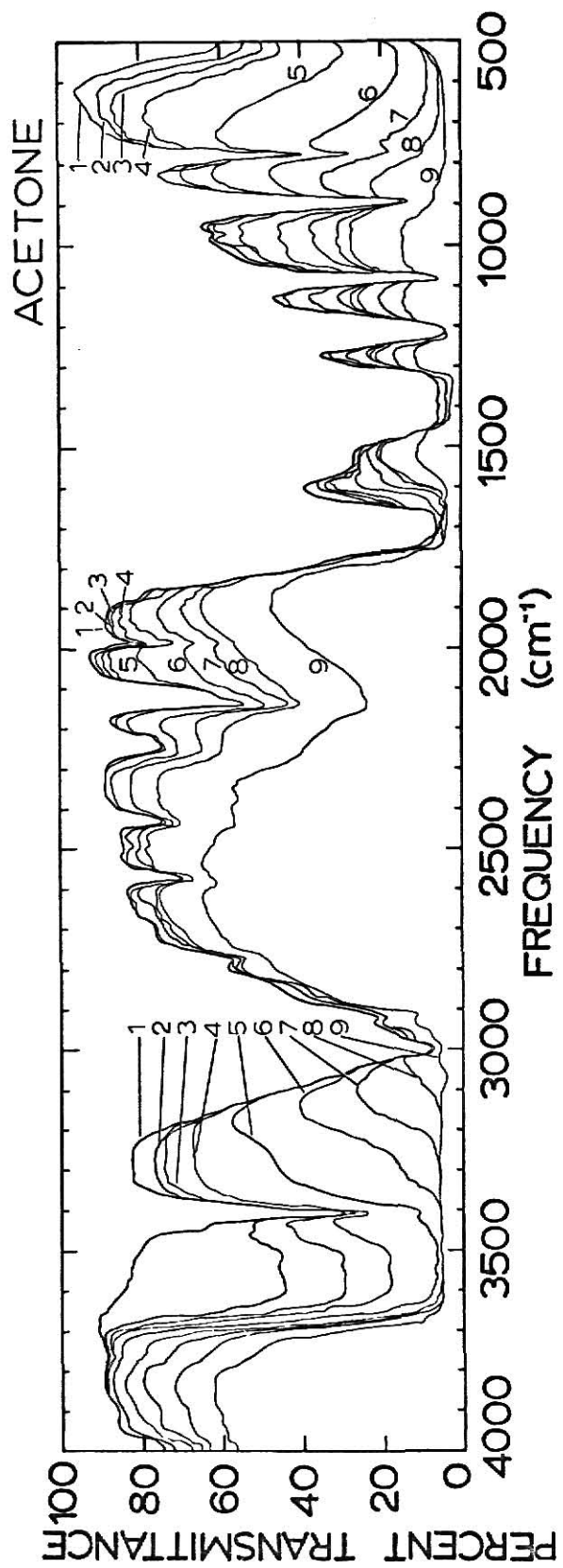
6 show the effect of the addition of increasing amounts of water to the acetone. The most obvious changes are the appearance of an intense water O-H stretching band centered at 3400 cm^{-1} that grows to cover the entire spectral region from 3700 to 2900 cm^{-1}, a strong water band that develops near 2100 cm^{-1} and also a broad band that grows in intensity at about 700 cm^{-1}. Since there is already an intense absorption band due to the acetone at 1800 cm^{-1}, the expected water ν_2 band at about 1650 cm^{-1} is almost obscured.

The development of the 3400 cm^{-1} water band is significant. We see in curves 2, 3, and 4 of Figure 6 two bands at 3600 and 3515 cm^{-1} that gradually move together as the concentration of water is increased. In curve 6 a shoulder appears that is apparently caused by a weak band at around 3260 cm^{-1}. As the water concentration increases further the band loses all individual features and becomes a single broad absorption band.

Intense solvent absorption often masks or distorts the water absorption bands being studied. In order to devise a method for minimizing solvent interference it is necessary to be in possession of certain facts concerning absorption of radiation by a sample.

If we consider the transmission of radiation of a given frequency and intensity I_0 through a sample of thickness x and absorption coefficient α and we ignore losses caused by reflection at window interfaces, we may write an expression for the intensity of the transmitted radiation:

$$I = I_0 \, e^{-\alpha x}. \tag{1}$$

We define the transmittance of the sample as

$$T \equiv \frac{I}{I_0} . \tag{2}$$

Then

$$T = e^{-\alpha x} . \tag{3}$$

If T_s is the transmittance of the pure solvent and T_{s+w} is the transmittance of the solvent plus water, we may write

$$T_{s+w} = e^{-\alpha_1 x} \tag{4}$$

and

$$T_s = e^{-\alpha_2 x} . \tag{5}$$

By dividing equation (4) by equation (5) and by taking the natural logarithm of this ratio we obtain:

$$Ln \frac{T_{s+w}}{T_s} = \alpha_2 x - \alpha_1 x . \tag{6}$$

We define

$$\alpha' \equiv \alpha_2 - \alpha_1 . \tag{7}$$

Finally

$$Ln \frac{T_{s+w}}{T_s} = \alpha' x . \tag{8}$$

Since the only difference between the pure solvent's transmission characteristics and that of the solvent plus water is the contribution of the water, we may identify α' as the absorption coefficient of the water in the sample and $\alpha' x$ as the absorbtance of a sample of thickness x at the frequency at which the ratio was taken.

In those spectral regions of the solvents in which water absorption is observed we may graphically take the ratio of the transmittance of the solvent- water mixture to the transmittance

of the pure solvent at various frequencies and plot this ratio
on the logarithmic axis of semilogarithmic graph paper versus
frequency on the other axis. This yields a plot of absorbtance
of the sample as a function of the frequency. In essence, we
are plotting the absorption due to the water in the solvent and
removing the effects of solvent absorption. Although this tech-
nique does not work in regions of intense solvent absorption, it
is of considerable use to visually aid in the determination of
band shape and location.

Figure 7 shows the log ratio plot of water in acetone in the
spectral region 3700 to 3100 cm^{-1}. At low concentrations of water
there are two weak bands. With 0.4% water (curve 1) the two bands
are at 3610 and 3515 cm^{-1}. As the water concentration increases
these two bands shift closer together into a single band. It is
reasonable to assume that the higher frequency band is the ν_3 band
and the lower frequency band is the ν_1 band as in water vapor.
In water vapor ν_3 and ν_1 are at 3756 and 3657 cm^{-1} respectively.
However, since ν_3 and ν_1 are apparently individually observable, it
shows that the interaction between the water and the acetone is
not as great as the water-water interaction. Strong interactions
involving a water molecule cause the ν_3 and ν_1 bands to shift to
lower frequencies. The ν_3 band is shifted a greater amount than
ν_1. This results in the two bands overlapping to form a single
broad band.

The ν_2 water band in acetone could not be given the log ratio
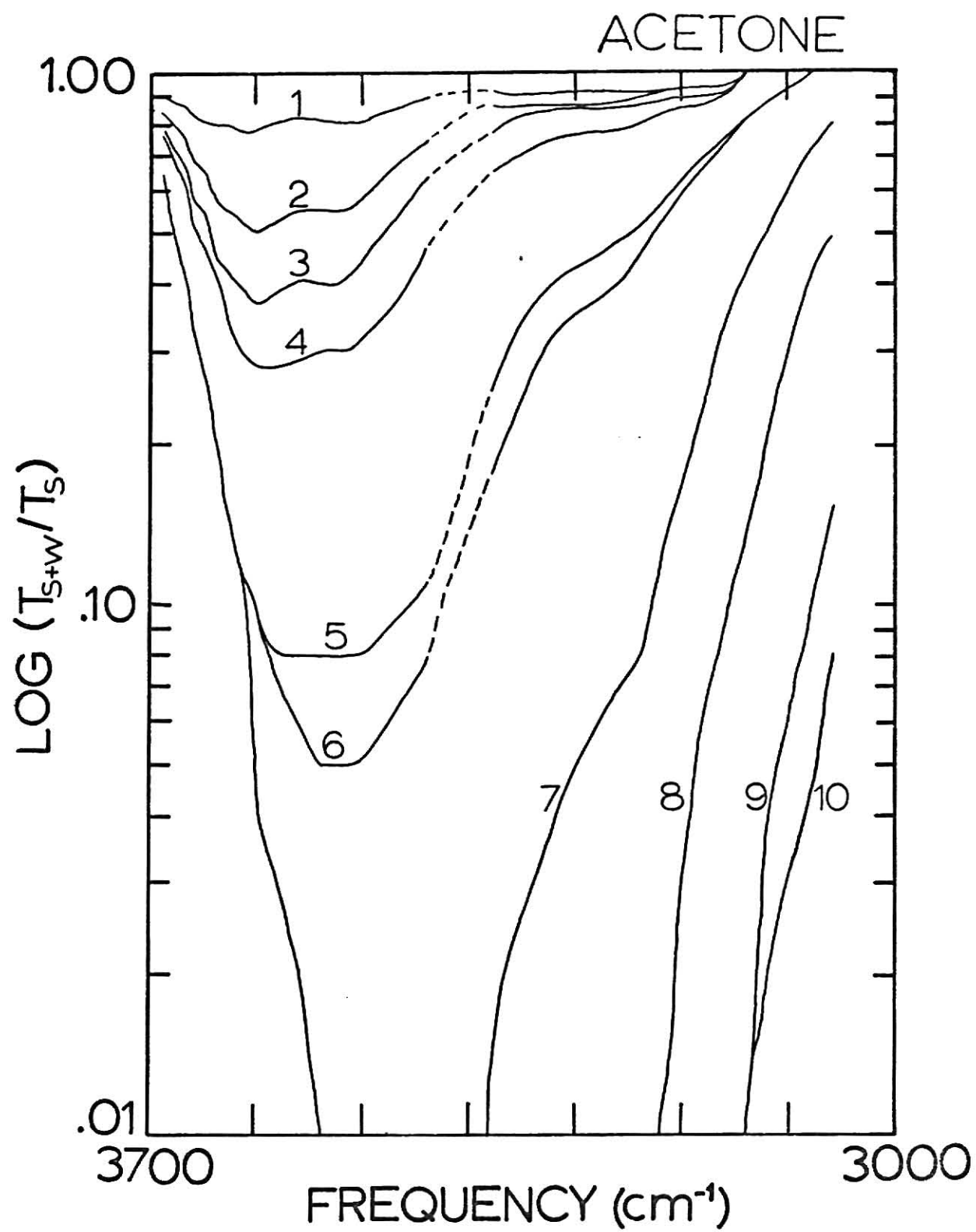analysis since it was almost completely obscured by an intense
acetone absorption band.

Figure 7. Log ratio plot of the ratio of the transmittance of acetone plus water to the transmittance of pure acetone, as a function of frequency in the spectral region 3700 to 3000 cm^{-1}. The amounts of water in the sample by volume are: (1) 0.4%, (2) 1.4%, (3) 2%, (4) 4%, (5) 8%, (6) 12%, (7)23%, (8) 33%, (9) 50%, (10) 80%.

ACETONE

FREQUENCY (cm⁻¹)

Figure 8. Log ratio plot of the ratio of the
transmittance of acetone plus water to the
transmittance of pure acetone, as a function
of frequency in the spectral region 1050 to
550 cm^{-1}. The amounts of water in the sam-
ples, by volume are: (1) 1.4%, (2) 4%,
(3) 12%, (4) 18%, (5) 23%, (6) 30%, (7) 33%,
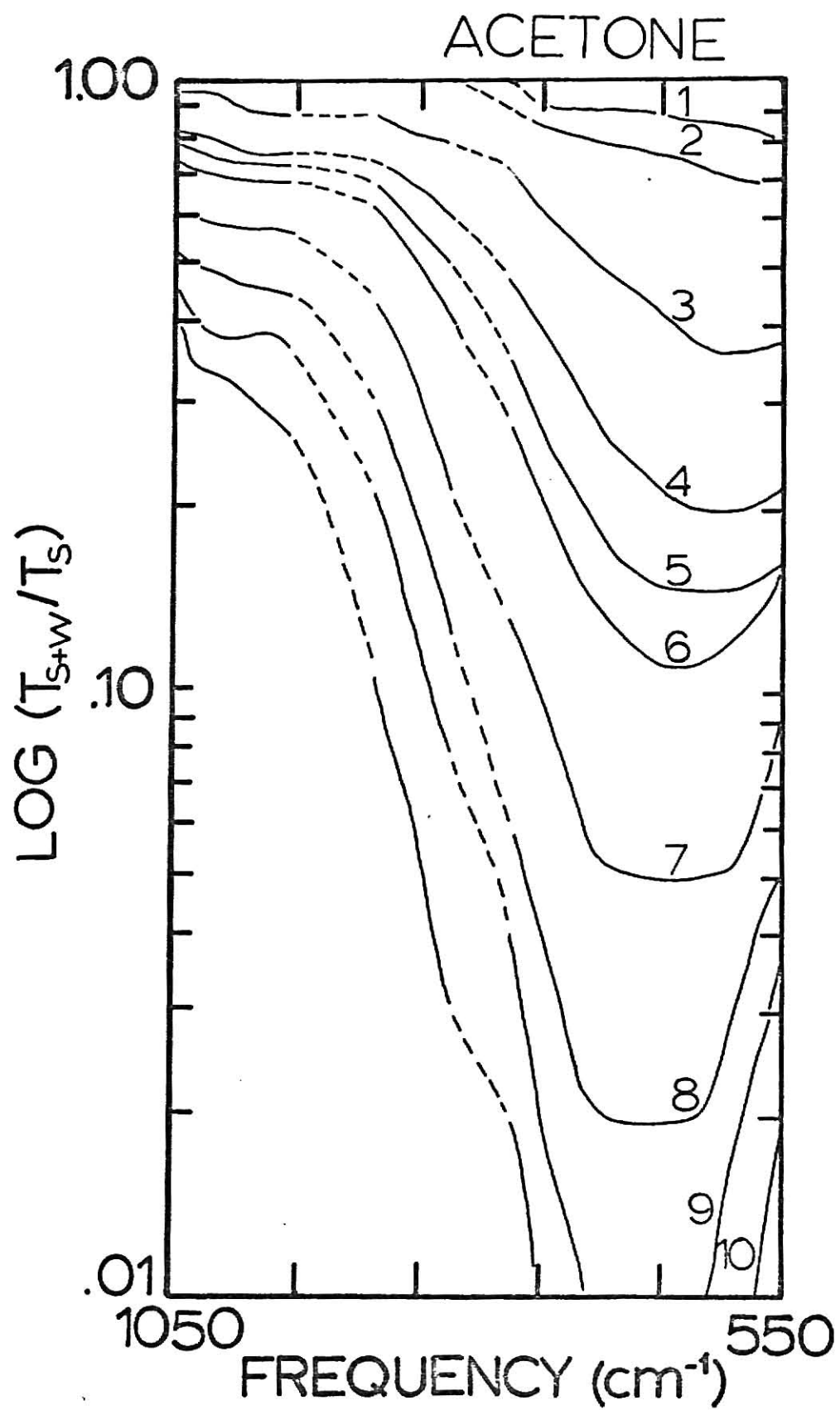(8) 41%, (9) 50%, (10) 70%.

ACETONE

Figure 8 shows the spectral region from 1050 to 550 cm^{-1} where we observe the ν_L band of water. At low concentrations of water the band is very weak and is located in the vicinity of 560 cm^{-1}. As the water concentration increases the band broadens and shifts to higher frequencies. It shifts to a maximum of 660 cm^{-1} at a 40% concentration of water. At water concentrations greater than this the band broadens but does not shift.

2. Acetonitrile

As with acetone, we see in curve 1 of Figure 9 that acetonitrile has numerous intense absorption bands across the entire spectral region. At low concentrations of water in the acetonitrile the two bands at 3620 and 3530 cm^{-1} in the spectrum are deepened and broadened by the water. At greater concentrations of water the band deepens further on the low frequency side until a broad band about 800 cm^{-1} wide is centered at about 3300 cm^{-1}.

The water ν_α band can be seen developing at about 2070 cm^{-1} in Figure 9 at greater concentrations of water even though the spectral region is partially obscured by acetonitrile bands. The water ν_2 band is free of interfering acetonitrile bands and clearly develops at 1625 cm^{-1}. The band does not shift in frequency as the concentration of water increases. The only change in this band is that it broadens considerably.

The spectral region below 1000 cm^{-1} has two sharp, intense acetonitrile bands, but they fail to obscure a water band that widens with increasing concentrations of water until it is a

Figure 9. Curve 1: Pure acetonitrile. The remaining curves are acetonitrile containing increasing amounts of water, measured by volume: (2) 0.9%, (3) 2%, (4) 5%, (5) 9%, (6) 16%, (7) 28%.
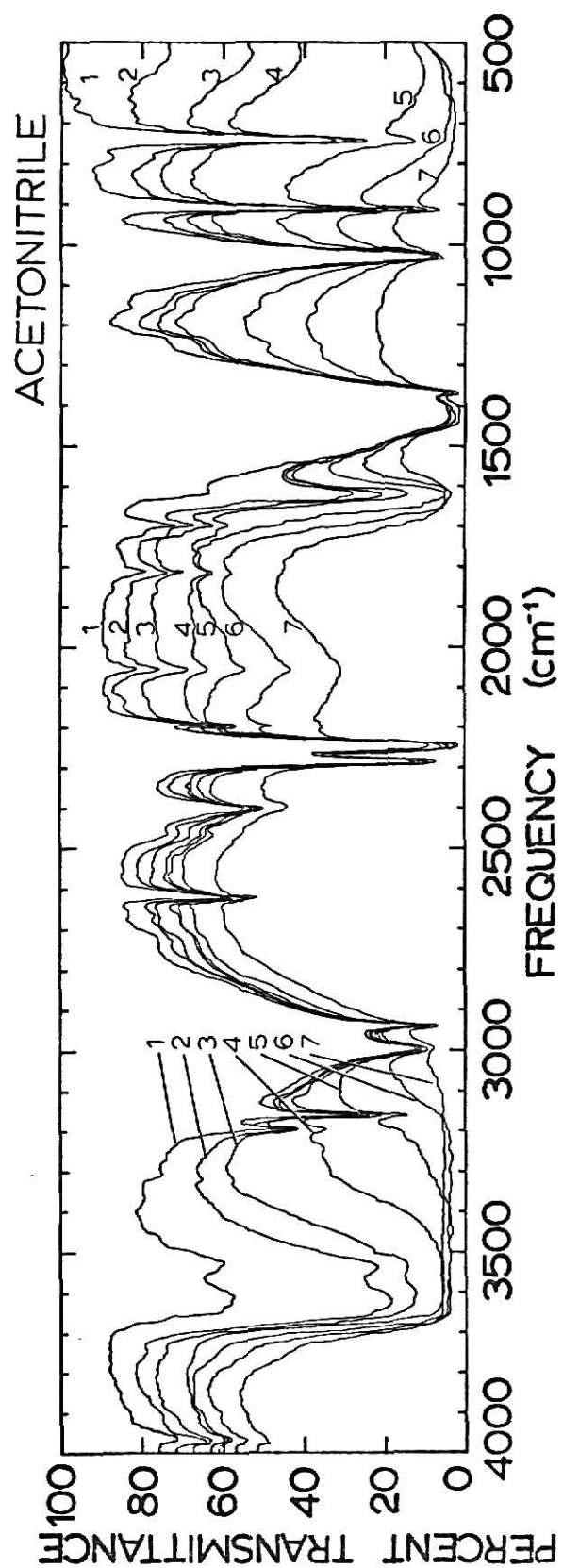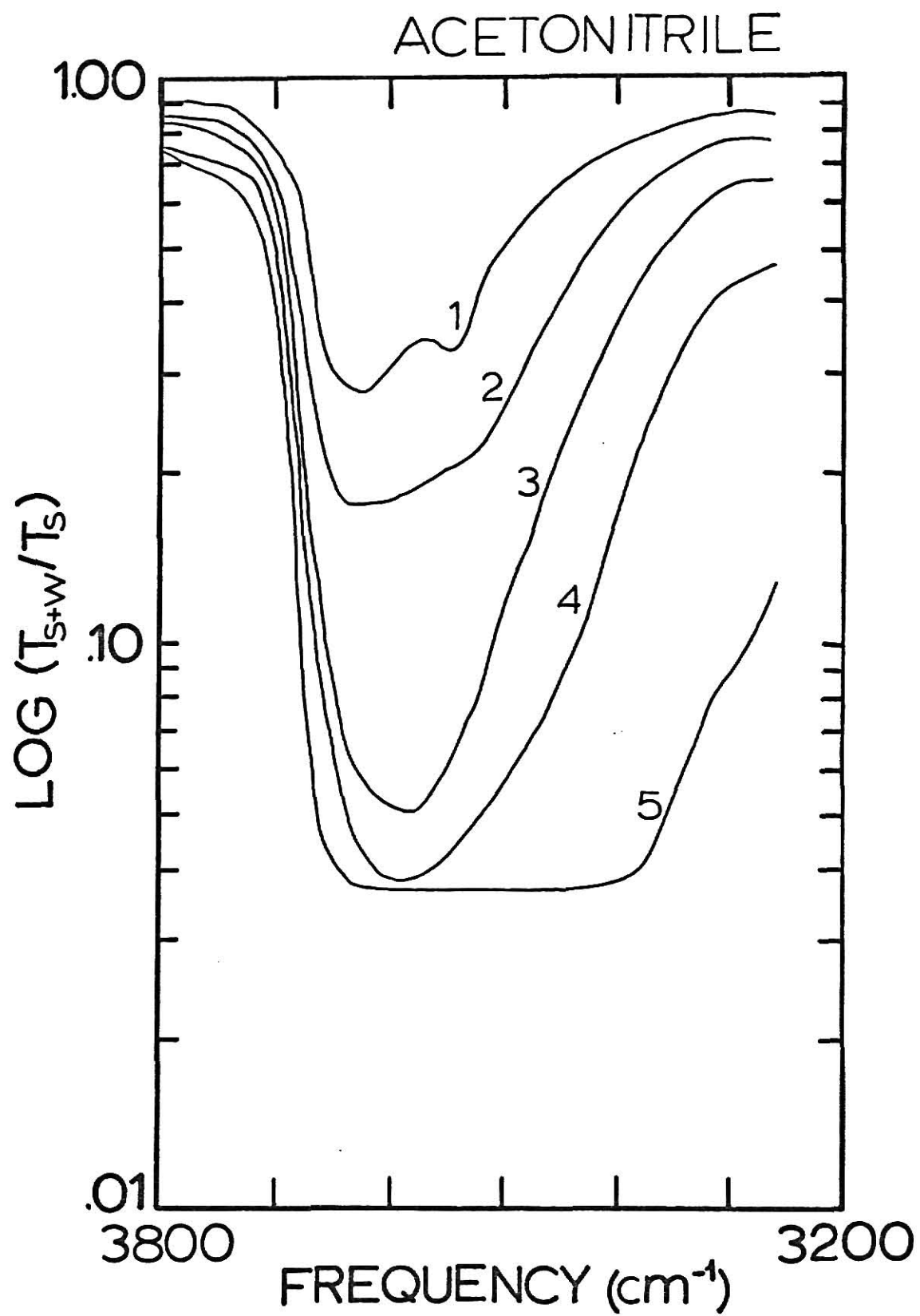
ACETONITRILE

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Figure 10. Log ratio plot of the ratio of the
transmittance of acetonitrile plus water to
the transmittance of pure acetonitrile as a
function of frequency in the spectral region
3800 to 3200 cm^{-1}. The amounts of water in
the samples, by volume are: (1) 0.9%, (2) 2%,
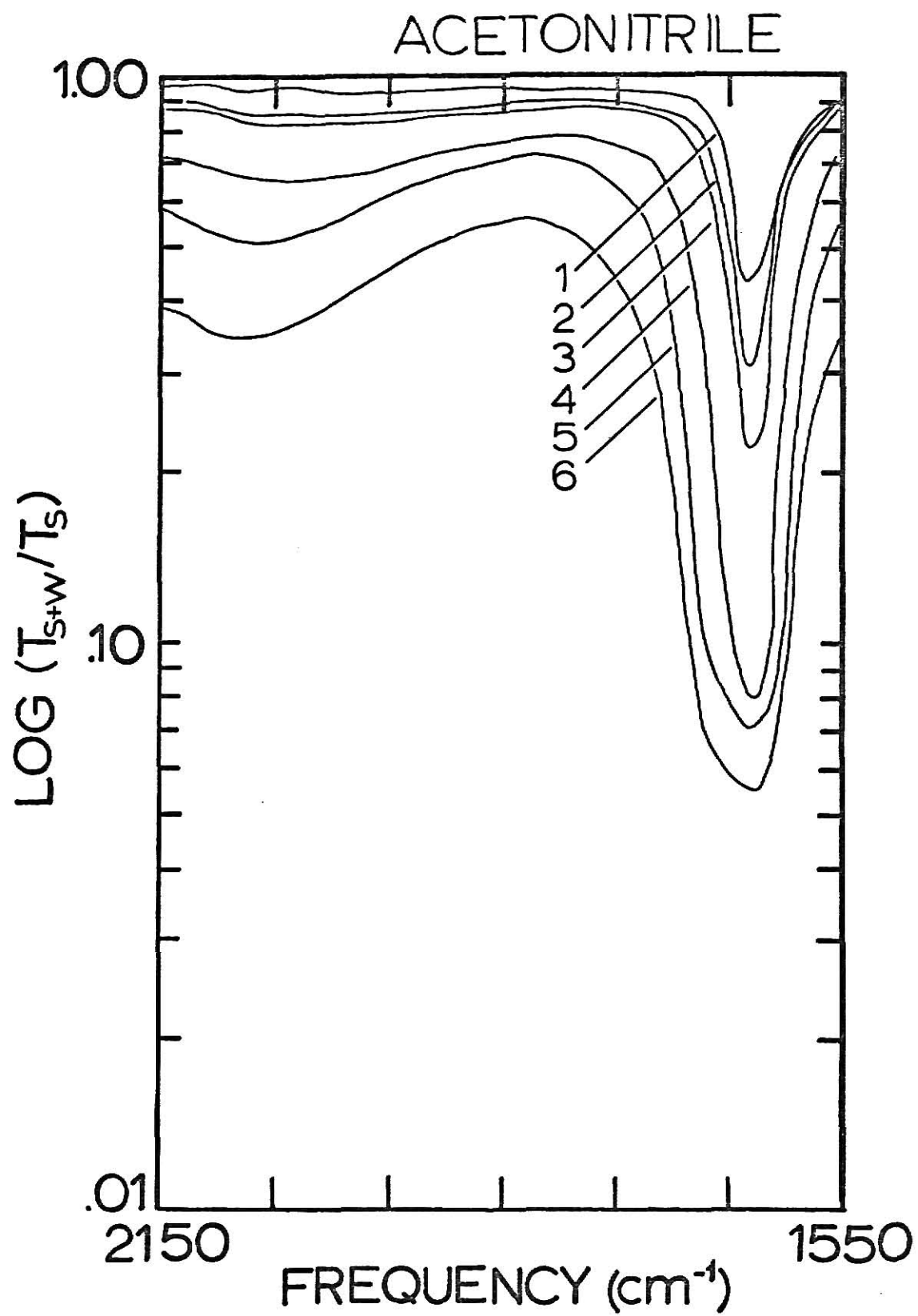(3) 3%, (4) 5%, (5) 9%.

ACETONITRILE

Figure 11. Log ratio plot of the ratio of the
transmittance of acetonitrile plus water to
the transmittance of pure acetonitrile as a
function of frequency in the spectral region
2150 to 1550 cm^{-1}. The amounts of water in
the samples, by volume are: (1) 0.9%, (2) 2%,
(3) 3%, (4) 9%, (5) 16%, (6) 28%.
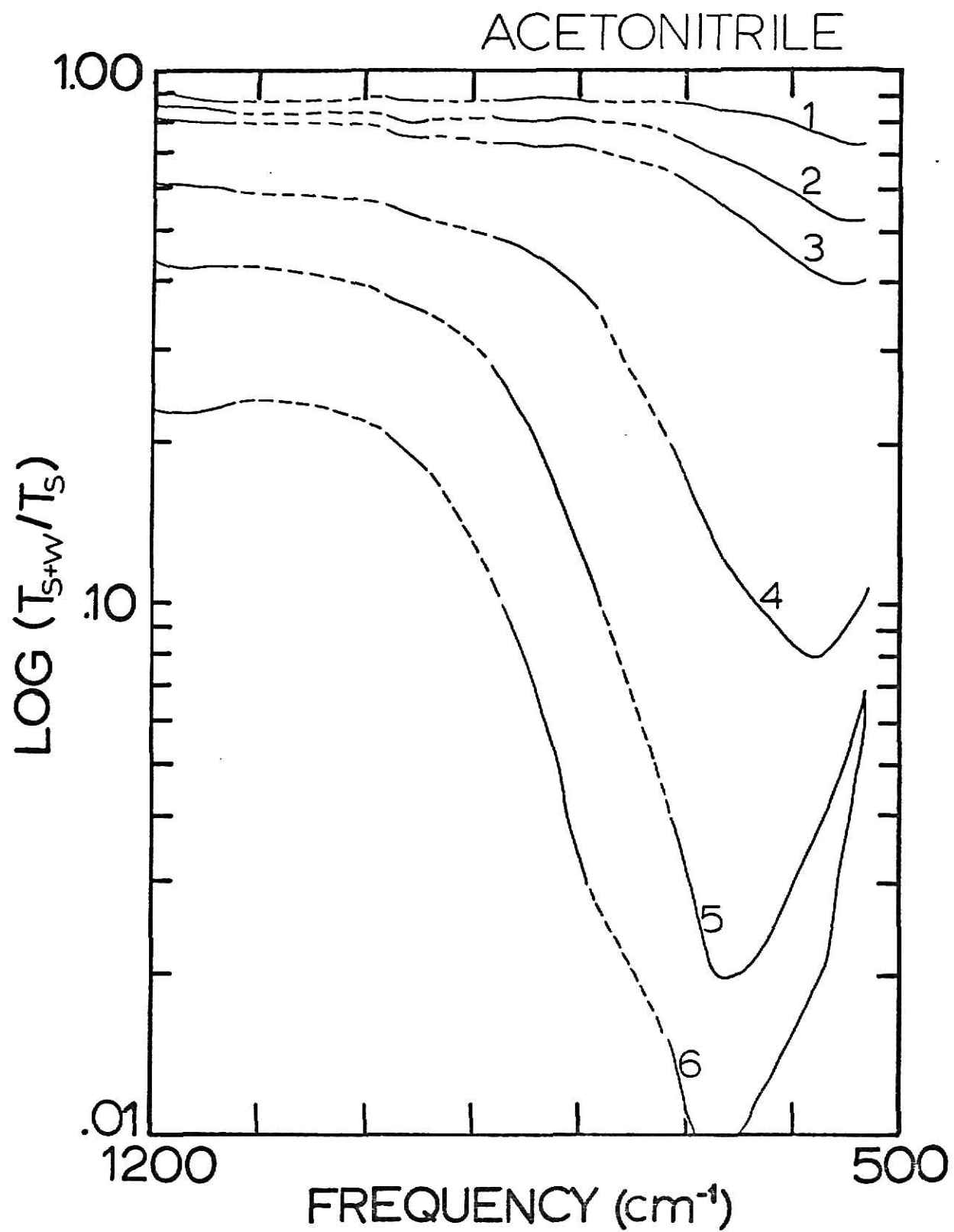
ACETONITRILE

Figure 12. Log ratio plot of the ratio of the
transmittance of acetonitrile plus water to
the transmittance of pure acetonitrile as a
function of frequency in the spectral region
1200 to 500 cm^{-1}. The amounts of water in
the samples, by volume are: (1) 0.9%, (2) 2%,
(3) 3%, (4) 5%, (5) 9%, (6) 16%.

ACETONITRILE

broad, intense band centered at about 700 cm^{-1}.

Figure 10 shows the log ratio plot of water in acetonitrile. At 0.9% water concentration (curve 1) there are two distinct bands at 3625 and 3545 cm^{-1}. These two bands probably correspond to the water ν_3 and ν_1 bands respectively. At only 2% water concentration (curve 2) these two bands are almost completely overlapping. This is in contrast to acetone, where the two bands were distinct until the water concentration exceeded 4%. The water molecules in acetonitrile are apparently so weakly associated with the acetonitrile molecules that they begin self association at considerably lower concentration of water than acetone. This implies that acetone bonds with water more strongly than does acetonitrile with water. This conclusion was also reached by Greinacher, et al.[2]

The log ratio plot of the spectral region from 2150 to 1550 cm^{-1} is shown in Figure 11 as further evidence that acetonitrile-water interaction is negligible. Even at low concentrations of water the position of the water ν_2 band is the same as in liquid water. As the water concentration increases the band broadens but does not shift.

Figure 12 shows the log ratio plot of the spectral region from 1200 to 500 cm^{-1}. It shows the growth of the ν_L band as water concentration increases but shows no new features not visible in the original spectrum in Figure 9.

3. Methanol

In Figure 13 is shown the spectrum of pure methanol. The

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Figure 13. Curve 1: Pure methanol. The remaining curves are methanol containing increasing amounts of water, measured by volume: (2) 3%, (3) 9%, (4) 16%, (5) 28%, (6) 44%, (7) 60%.

METHANOL
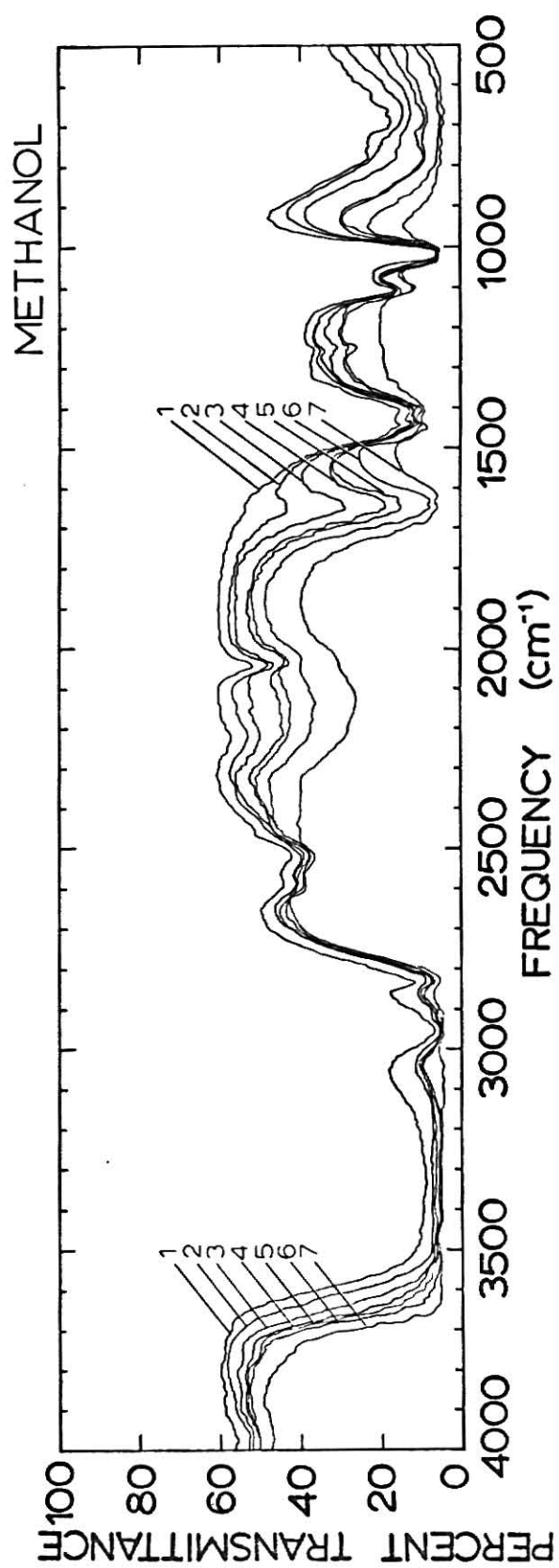
spectrum has a broad band centered at around 3300 cm^{-1} due to O-H stretching and an overlapping band at 2900 cm^{-1} due to C-H stretching. The intensity of these two bands almost completely obscures the water bands that we would expect to appear when water is added to the methanol. Curves 2 through 7 show little change in this spectral region as the concentration of water increases.

Fortunately the spectral region in which we observe the ν_a and ν_2 bands of water is almost completely free of interfering methanol absorption bands. Curves 3 through 7 show the ν_a band appearing at about 2150 cm^{-1} as the water concentration increases. Similarly, the ν_2 band appears at 1650 cm^{-1} at low concentrations of water. It gradually shifts to 1630 cm^{-1} at higher concentrations of water.

There is a broad band due to the methanol absorption centered at 700 cm^{-1}. As water is added, this band is broadened and deepened but remains centered at about 700 cm^{-1}.

The only spectral region that could be given the log ratio plot analysis is shown in Figure 14. The spectral region from 2350 to 1550 cm^{-1} includes the water ν_a and ν_2 bands. At low concentrations of water the ν_2 band is at 1650 cm^{-1}. In liquid water ν_2 is at 1620 cm^{-1}. The 30 cm^{-1} shift to higher frequencies at low water concentrations may indicate significant hydrogen bonding of the water and methanol molecules.[18] As the water concentration increases, the band shifts to lower frequencies and becomes more nearly like the liquid water band. This shift to lower frequencies is reasonable since the sample is, in fact,

Figure 14. Log ratio plot of the ratio of the
transmittance of methanol plus water to the
transmittance of pure methanol as a function
of frequency in the spectral region 2350 to
1550 cm^{-1}. The amounts of water in the sam-
ples, by volume are: (1) 3%, (2) 9%, (3) 16%,
(4) 28%, (5) 44%, (6) 60%.

METHANOL
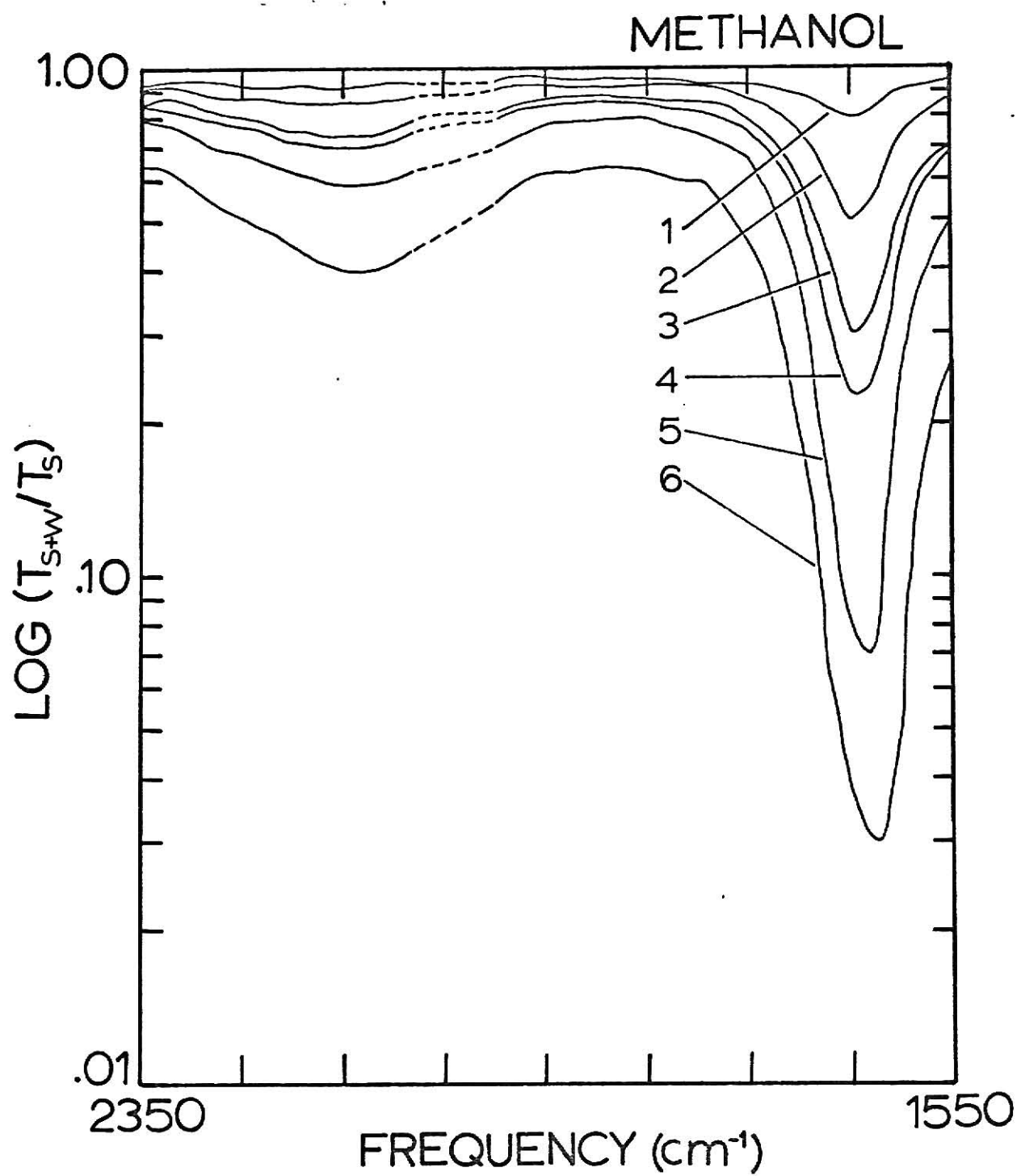
mostly liquid water.

The water ν_α band in Figure 14 also shifts to lower frequencies as the water concentration increases. This occurs since ν_α is dependent upon ν_2 and ν_L. Although we did not observe the ν_L band we assume that ν_L shifts to higher frequencies also. The ν_α band eventually shifts to 2130 cm^{-1}. Its position is almost the same as the ν_α band in liquid water.

4. Summary of Organic Solvents Results

The three organic solvents studied demonstrated rather different abilities to interact with water. The principal indicator of water-solvent interaction was the shifting and evolution of the various water absorption bands. To facilitate the observation of the water absorption bands we graphically removed the effect of solvent absorption by taking the ratio of the transmittance of the solvent plus water to the transmittance of the pure solvent as a function of frequency. We plotted this ratio on a semilogarithmic graph. This procedure was effective in spectral regions in which solvent absorption was not strong.

Acetonitrile appears to interact only negligibly with water. Water absorption bands in acetonitrile are found at the same frequency as in liquid water. The location of the water bands does not shift as water concentration in the solvent is increased.

Acetone seems to interact with water moderately well. At low concentrations of water the ν_3 and ν_1 fundamental bands can be observed. This is indicative of water-acetone interaction rather than water-water interaction. As the water concentration

In the acetone increases these two bands shift to lower frequencies and merge into a single band as water-water interaction becomes predominant.

Methanol apparently interacts quite strongly with water. At low concentrations of water the ν_2 fundamental band was seen to be shifted to higher frequencies than in liquid water. This shift usually is indicative of significant hydrogen bonding between the methanol and water molecules. At greater concentrations of water the ν_2 band shifts to lower frequencies and becomes nearly like the liquid water band.

In view of the apparent ability of methanol to form strong hydrogen bonds, we judge it to interact with water the most strongly of the three organic solvents studied. Next in order of strength of interaction is acetone, and finally, acetonitrile, which interacted negligibly with water.

C. Organic Films

1. Agar

Figure 15 shows the absorption spectrum of an agar film approximately 30 microns thick. It shows characteristic O-H stretching at around 3350 cm^{-1} and C-H stretching at 2900 cm^{-1}. The absorption band at 1630 cm^{-1} can be attributed to an agar absorption band and to an overlapping ν_2 band of water. The fairly broad band near 2100 cm^{-1}, which is probably the water ν_a band, indicates that there is a fair amount of water in the film. In the spectral region below 1500 cm^{-1}, the spectrum of

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Figure 15. The spectrum of an agar film about
30 microns thick.

67
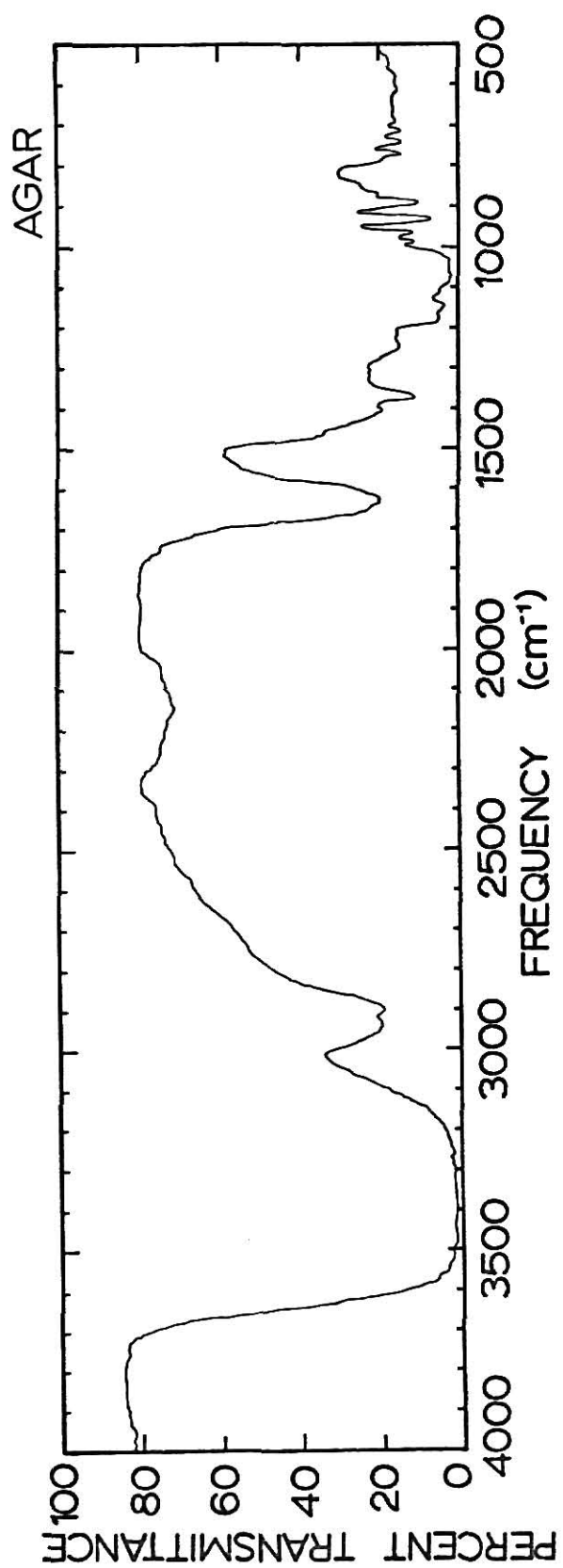
AGAR

the agar samples is characterized by numerous and complex absorption bands.

The agar spectrum is free from significant absorption only in the water ν_α spectral region. Thus, the study of the water in agar is limited to observation of this single band.

Figure 16 shows the development of the water ν_α band as the amount of water in an agar film increases. It is interesting to note that there is a small shift to higher frequencies as the concentration of water is increased. At 20% water the band is at 2140 cm^{-1}. At 55% water it is at 2150 cm^{-1}.

In the cases in which we had no particular interest in the amount of water in the film per se, we invariably observed that the ν_α band was located at about 2150 cm^{-1}; therefore, it seems likely that the water concentration in these films was on the order of 50%. This is apparently the amount of water in the film at equilibrium with the 50-60% relative humidity that prevailed in the laboratory during the period of data taking. For purposes of comparison in this study we shall designate 2150 cm^{-1} as the location of the ν_α water band in agar. The ν_α band in liquid water is found 2120 cm^{-1}.

Earlier workers have studied the effect of the addition of ions to water on the infrared spectrum of water.[19,20] Both positive and negative ions cause the water bands to shift, but positive ions cause smaller shifts. The spectral effect of the presence of ions in the water depends upon the ratio of the ionic charge to the ionic radius. Studies of aqueous solutions involving a sequence of ions of equal charge show that the larger ions

shift the water bands in a way similar to the shift of the water bands produced by elevation of the temperature of pure water. Smaller ions shift the water bands in a way similar to the shift of the water bands caused by lowering the temperature of pure water. An increase in the frequency of ν_α is indicative of a more ordered structure than liquid water, whereas a decrease in the frequency of ν_α indicates a less ordered structure than liquid water. Draegert and Williams[19] refer to ions which cause water to appear to be in a more ordered configuration as "structure makers" and to those ions which make water appear to be in a less ordered configuration as "structure breakers".

The water ν_α band in pure agar is already shifted 30 cm^{-1} higher in frequency that the ν_α band in liquid water. Addition of the strong electrolyte potassium fluoride to agar films causes the ν_α band to shift still further to 2190 cm^{-1} as shown in Figure 17. The fluoride ion has an ionic radius of only 1.33 Å[21] and a charge of -1e. This charge distributed over the small ion makes the electrostatic field about the ion considerably more intense that the electrostatic fields of the ions of the rest of the halides. The chloride, bromide, and iodide ions all have a charge of -1e but this charge is distributed over ions 1.81, 1.96 and 2.20 Å in radius respectively.

The water ν_α band in agar in the presence of the chloride ion appears shifted 10 cm^{-1} lower in frequency than the band in pure agar. The bromide ion causes the band to shift 50 cm^{-1} lower and the iodide ion causes a shift 70 cm^{-1} lower.

The ν_2 band in water generally shifts only a small amount in

Figure 16. The location of the water associ-
ational band ν_a in an 80 micron agar film,
as a function of the amount of water in the
film. The amounts of water in the film,
measured by weight are: (1) 0% (essentially
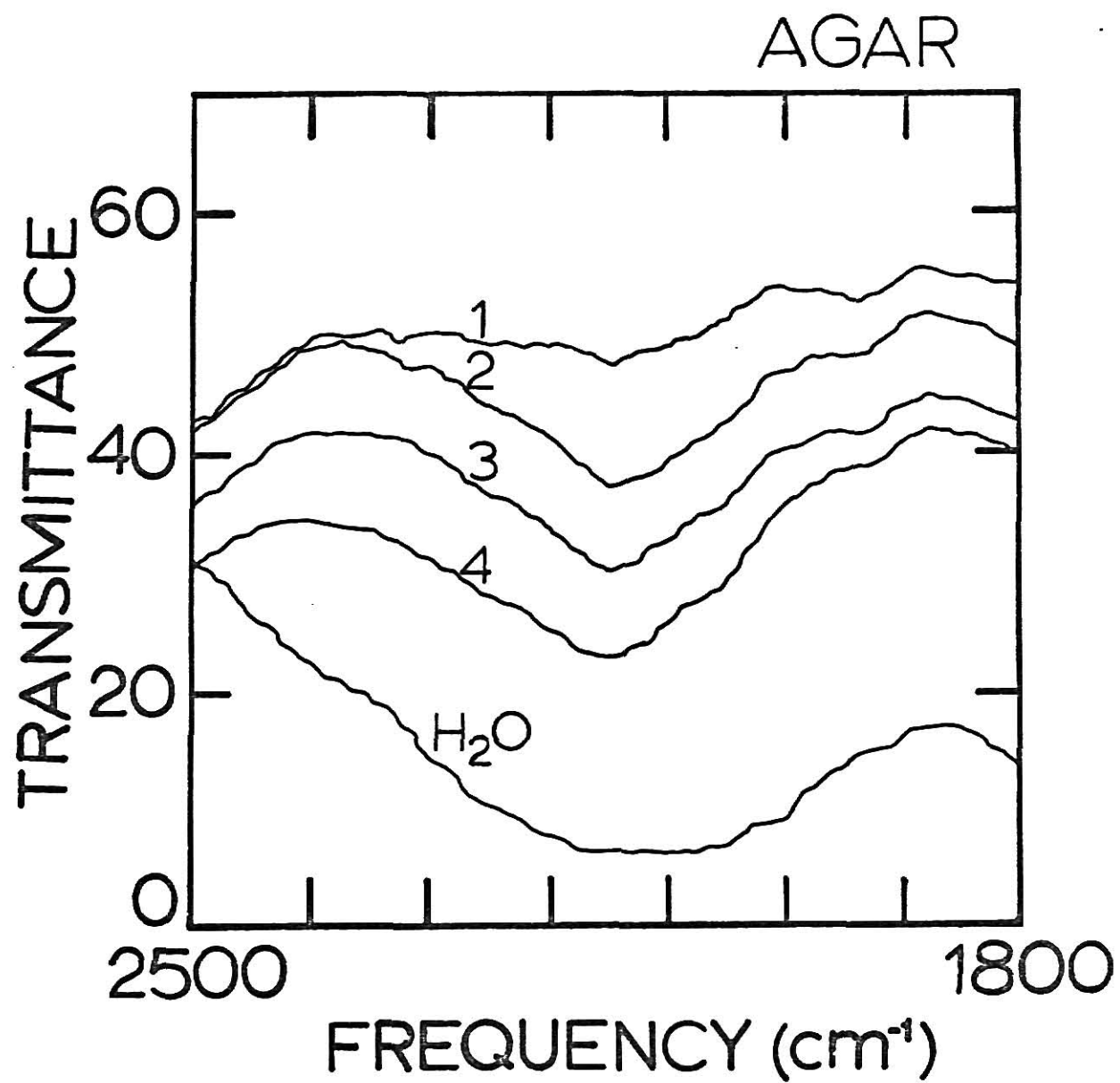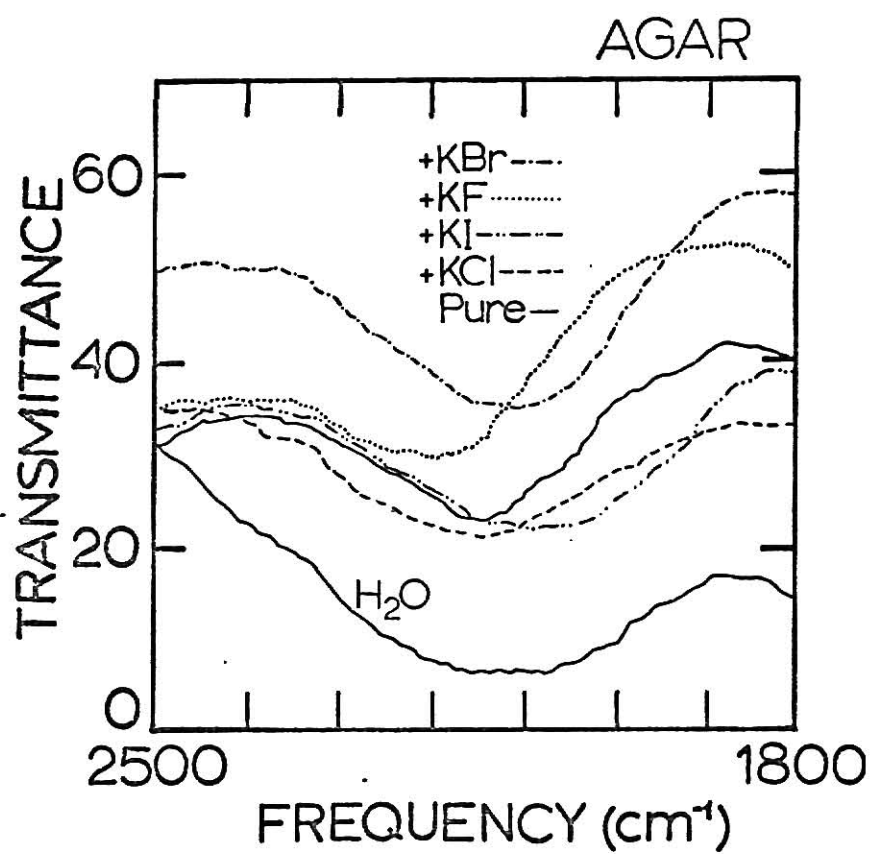dry), (2) 20%. (3) 28%, (4) 55%.

Figure 17. The effect of the addition of various potassium halide salts on the location of the water associational band ν_a of agar.

AGAR

+KBr —·—
+KF ·······
+KI —··—
+KCl ———
Pure —

response to a changing environment. Since the ν_α band is shifted significantly by the addition of ions we assume that this shift is, for the most part, a result of a corresponding shift of the ν_L band in agar. In the case of the ν_2 and ν_L bands a more ordered configuration results in a shift of these bands to higher frequencies and a less ordered configuration would result in a shift to lower frequencies. In Draegert and Williams's terminology the fluoride ion is a "structure maker" and the chloride, bromide, and iodide ions are "structure breakers".

Table 2. Shifts of the water associational band ν_α in agar films in response to the addition of various potassium halide salts.

Salt	ν (cm^{-1})	$\Delta\nu$ (relative to the 2120 cm^{-1} ν_α band in pure water)	Equiv. Temp. (^oC)
KF	2190	+70	-56
Pure Agar	2150	+30	-10
KCl	2140	+20	1
KBr	2100	-20	49
KI	2080	-40	71

The results obtained with the solutes are similar to the results of Draegert and Williams[19] who worked with aqueous solutions. This would seem to suggest that the water molecules in the films acted much as they would in liquid water. Draegert[22] found that the observed shifts of the frequency of the minima of transmittance of the ν_α band in liquid water at various

temperatures in the range 5°C to 75°C were consistent with a shift of -0.86 cm^{-1}/Cdeg. By comparison of the observed frequencies of the bands in the various agar films to the frequency of the band in liquid water we were able to estimate the "equivalent temperature" of the water in the agar films. The ν_α band in liquid water appears at 2120 cm^{-1} at 24°C. Since the ν_α band in pure agar is at about 2150 cm^{-1}, a shift of 30 cm^{-1} higher in frequency than ν_α in liquid water, we compute an equivalent temperature of approximately -10°C. That is, the water in a pure agar film is ordered to the extent that it resembles pure water cooled to near -10°C. The shifts of the ν_α band in the other agar samples are summarized in Table 2. The chloride, bromide, and iodide ions cause shifts of the agar ν_α band of +20, -20, and -40 cm^{-1} respectively, relative to the frequency of the liquid water ν_α band. One should not forget, however, that these shifts are all observed in the presence of the potassium ion. We assume that the contribution of the potassium ion is the same in all of the samples. These shifts correspond to equivalent temperatures of the water in the various agar films of 1°C for the agar and KCl film, 49°C for the agar and KBr film, and 71°C for the agar and KI film.

The concept of equivalent temperature, which was first proposed by Bernal and Fowler[23] is of great use for x-ray diffraction studies; however, the application to our infrared studies sometimes yields surprising results. For instance, the frequency of the ν_α band of the agar film with potassium fluoride is 70 cm^{-1} higher than the ν_α band in liquid water. This implies an

equivalent temperature of about -56°C. By using the position of the ν_α band as a measure of the ordered nature of the water structure, we conclude that the water in the agar film with potassium fluoride present is considerably more ordered than liquid water at 0°C and is more nearly like ice, in which ν_α is found at about 2200 cm^{-1} for samples near 0°C.[24]

2. Gelatin

The spectrum of a thin film of dry gelatin is shown in Figure 18. The spectrum is similar in many respects to the agar spectrum since it, too, has a strong O-H stretching band centered at 3300 cm^{-1}, a C-H stretching band at 2900 cm^{-1} and a spectral region from 2500 to 1800 cm^{-1} free from absorption bands. Since gelatin is a protein we expect that the band centered at 3300 cm^{-1} results, in part, from absorption caused by N-H groups also. These groups characteristically contribute absorption bands in the spectral region from 3500 to 3100 cm^{-1}.[25] At frequencies below 1800 cm^{-1} the spectrum contains numerous and complex absorption bands.

Figure 19 shows the effect of the addition of the potassium halide salts to gelatin upon the water ν_α band. The ν_α band in the pure gelatin film is at 2130 cm^{-1}. Although the magnitudes of the shifts of the ν_α band in gelatin in response to the various ions are different from the shifts observed in agar, the direction of the shifts is identical. The fluoride ion causes a shift 70 cm^{-1} higher in frequency relative to the 2130 cm^{-1} band in pure gelatin and 80 cm^{-1} higher relative to the 2120 cm^{-1}

Figure 18. The spectrum of a gelatin film about
10 microns thick.
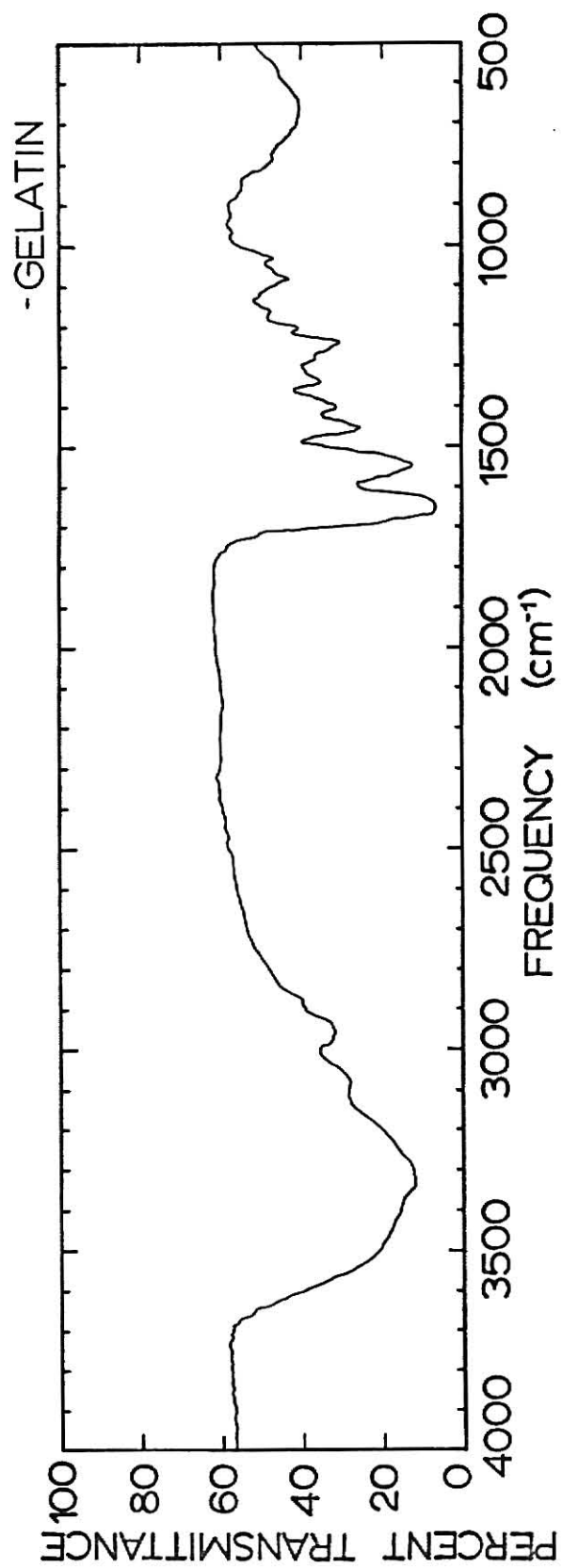
-GELATIN

ν_α band in liquid water. The chloride, bromide, and iodide ions cause shifts of 10, 60, and 90 cm^{-1} to lower frequencies, respectively.

As with agar, we observe that the water molecules in the gelatin films behave much like they would in liquid water in response to the addition of ions.

The fluoride ion shifted the ν_α band to about 2200 cm^{-1}, which is the same frequency as the ν_α band in ice at -7°C[24] and corresponds to an equivalent temperature of -68°C. As a contrast, the iodide ion shifted the ν_α band to 2040 cm^{-1}, which resembles the ν_α band in pure water which has been heated to a temperature of about 118°C.

Table 3. Shifts of the water associational band ν_α in gelatin films in response to the addition of various potassium halide salts.

Salt	ν(cm^{-1})	$\Delta\nu$(relative to the 2120 cm^{-1} ν_α band in pure water)	Equiv. Temp. (°C)
KF	2200	+80	-68
Pure Gelatin	2130	+10	13
KCl	2120	0	25
KBr	2070	-50	83
KI	2040	-80	118

Table 3 summarizes the effects of the various ions on the ν_α band in gelatin. The fluoride, chloride, bromide and iodide ions cause the gelatin ν_α band to shift +80, 0, -50, and -80 cm^{-1}

80

Figure 19. The effect of the addition of various potassium halide salts on the location of the water associational band ν_a of gelatin.
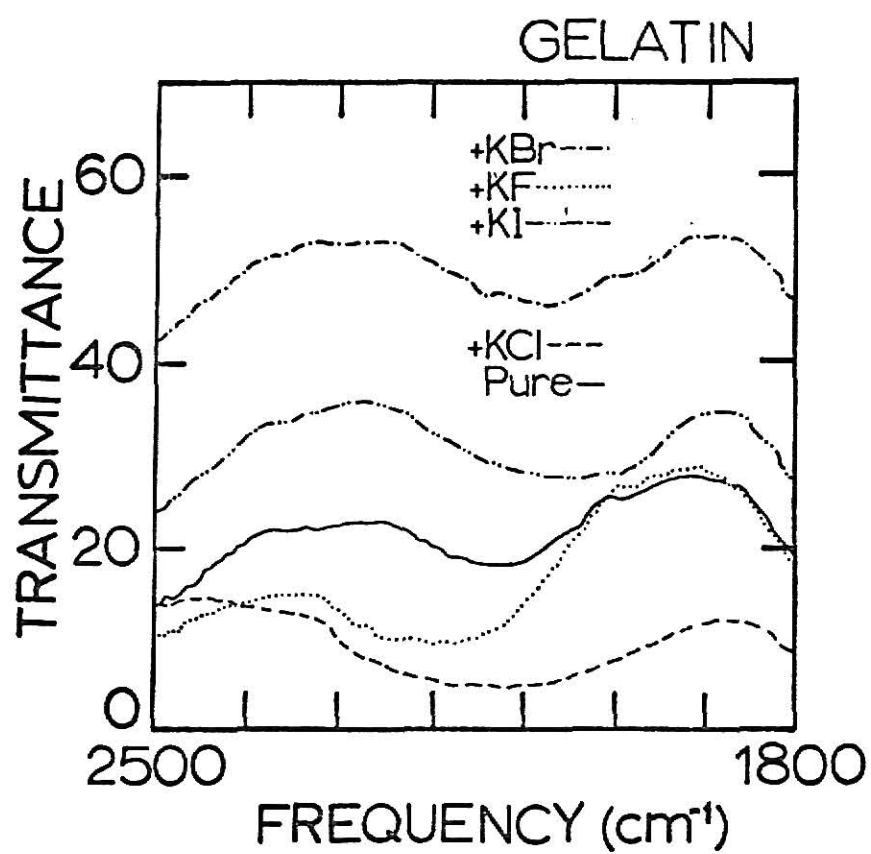
respectively, relative to the liquid water ν_a band. These shifts correspond to equivalent temperatures of the water in the various gelatin films of 25°C for gelatin and KCl, 83°C for gelatin and KBr, and 118°C for gelatin and KI.

3. Summary of the Organic Films Results

We found in our study of organic films that an agar film is extremely hygroscopic and tends to lose or gain water until it reaches equilibrium with water vapor in the air around it. Gelatin films, on the other hand, show little inclination to absorb or to give off water after they have dried into a film.

The ν_a band in pure agar and gelatin is shifted to higher frequencies than the ν_a band in pure water. The ν_a band in pure water is found at 2120 cm^{-1}, whereas, ν_a in agar is at 2150 cm^{-1} and at 2130 cm^{-1} in gelatin. The addition of potassium halides to agar and gelatin causes the water ν_a band in each film to shift from the position that the ν_a band usually occupies in the pure sample. The direction and magnitude of this shift seems related to the ionic size and charge. The fluoride ion in the presence of the potassium ion shifts the ν_a band to higher frequencies in both types of film This shift suggest greater ordering of the water molecules in the films. The chloride, bromide, and iodide ions in the presence of the potassium ion causes shifts of the ν_a band to lower frequencies than the frequency of the ν_a band in the pure films. The magnitude of this shift to lower frequencies increases with increasing ionic radius.

The similarity of our results to the results of studies of

the effect of the addition of ions to liquid water suggests that the water in the agar and gelatin films is not significantly associated with the molecules of the films but act much like liquid water at different temperatures. The fluoride and chloride ions causes the water ν_a band in agar films to resemble the ν_a band in pure water that has been cooled below the freezing temperature but is not ice. The bromide and iodide ions cause the ν_a band in agar to resemble the ν_a band in water that has been heated; e.g., the iodide ion causes the ν_a band in agar to appear like the ν_a band in pure water heated to 71°C. The effect of the ions in the gelatin films is more marked. The fluoride ion causes the ν_a band in gelatin to resemble the ν_a band in ice. The iodide ion causes the ν_a band in gelatin to resemble the band in pure water that has been heated to about 118°C.

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Appendix: The Spectra of Glucose and

Certain High Purity Polymers of Glucose

Several high purity sugar samples were provided by Pro-
fessor John Johnson of the Department of Grain Science and
Industry, Kansas State University. These samples were pre-
pared by Miss Rujira Srisuthep as part of her research toward
the degree of Master of Science in Food Science. The sugars
were unique in the sense that they had never before been iso-
lated into chemically pure species. In cooperation with Miss
Srisuthep and Professor Johnson we attempted to provide infra-
red spectra for these sugars in a preliminary effort to deter-
mine some of the physical characteristics of the sugars. In-
frared spectroscopy is widely used in "fingerprinting" chemical
compounds and the expectation was that the infrared spectra of
these sugars would prove of value.

The sugar samples consisted of glucose and high-purity
polymers of glucose ranging from two glucose units in a chain
(maltose) to twelve units in a chain (maltododecaose) inclu-
sively. Due to the unwieldy nomenclature of the sugars they
will be referred to hereafter in the report in terms of the
number of glucose units in the sugar prefexed by the letter G
for "glucose". Thus, glucose is G-1, maltose is G-2, and so on.

The sugars G-3 through G-12 were separated from corn starch
hydrolyzate on a 12 foot charcoal-Celite column. The G-3 and
G-4 polymers were eluted with 15% and 20% aqueous solutions of
ethanol respectively. The G-5, G-6, and G-7 polymers were

admixed together in the fraction eluted with the 20% ethanol solution and were recovered separately. The G-8, G-9, G-10, G-11, and G-12 polymers were eluted from the column using 25, 30, 35, and 50% solutions of ethanol. These separated eluates were removed from solution by evaporating the ethanol solution under vacuum. The dried partially separated sugars were dissolved in an n-propanol-ethyl acetate-water solvent and separated into chromatographically pure, white, amorphous sugars by paper chromatography.[26]

Since the sugar samples were of a light and fluffy texture not unlike cotton candy, it was necessary first to reduce the sample to a fine powder with a "Wig-L-Bug" shaker before a satisfactory mull could be made.

We were warned that the sugar samples were extremely hygroscopic, so we exercised care in the preparation of the samples to minimize the possibility of contamination by atmospheric moisture. These precautions included heating the "Wig-L-Bug" shaker capsule to remove any moisture and using great haste in the transfer of the samples from their tightly sealed bottles to the shaker capsule.

After having been pulverized for five minutes, one half of the powdered sample was removed from the shaker capsule and immediately mixed with hexachloro 1,3 butadiene and pressed into a thin film between two 25mm-in-diameter calcium fluoride windows. The windows were clamped into an aluminum holder and placed in the sample beam of the spectrometer. The spectra were recorded on the Perkin-Elmer Model 421 Spectrophotometer. In

this manner the samples were prepared for the recording of their spectra in the spectral region from 4000 to 2000 cm^{-1}.

The spectrum from 2000 to 500 cm^{-1} was recorded by using the remaining half of the powdered sample. The sample was mixed with a small amount of Vaseline Petroleum Jelly in an agate mortar and pestle. A small amount of this mixture was squeezed into a thin film between two silver chloride windows, clamped into a holder, and then placed in the sample beam of the spectrometer.

The butadiene mull was used in the spectral region from 4000 to 2000 cm^{-1} because it contributed no obscuring absorption bands to the spectrum in this spectral region. The spectrum is shown in Figure 20. It could not, however, be used in the spectral region below 2000 cm^{-1} because it has numerous absorption bands in this spectral region. Even though Vaseline has several absorption bands in this spectral region also, the bands are not nearly as numerous as in butadiene and they do not seriously obscure this spectral region. The Vaseline spectrum is shown in Figure 20.

All of the spectra are very similar in their major details. The spectra of G-1 and G-2 in Figure 21 have a strong O-H stretching band centered at about 3300 cm^{-1}. In G-3 through G-12 this band is centered at about 3350 cm^{-1}. The C-H stretching band at 2900 cm^{-1} in G-1 and G-2 is composed of several sharp bands. In G-3 through G-12 this band is a single featureless band at 2900 cm^{-1}.

The G-1 and G-2 spectra shown in Figure 21 have several minor differences in band structure in the spectral region from 1500 to 700 cm^{-1} that make them easily distinguishable. As

Figure 20. The spectra of Vaseline Petroleum Jelly and hexachloro 1,3 butadiene.

ILLEGIBLE DOCUMENT

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DOCUMENT(S) IS OF
POOR LEGIBILITY IN
THE ORIGINAL
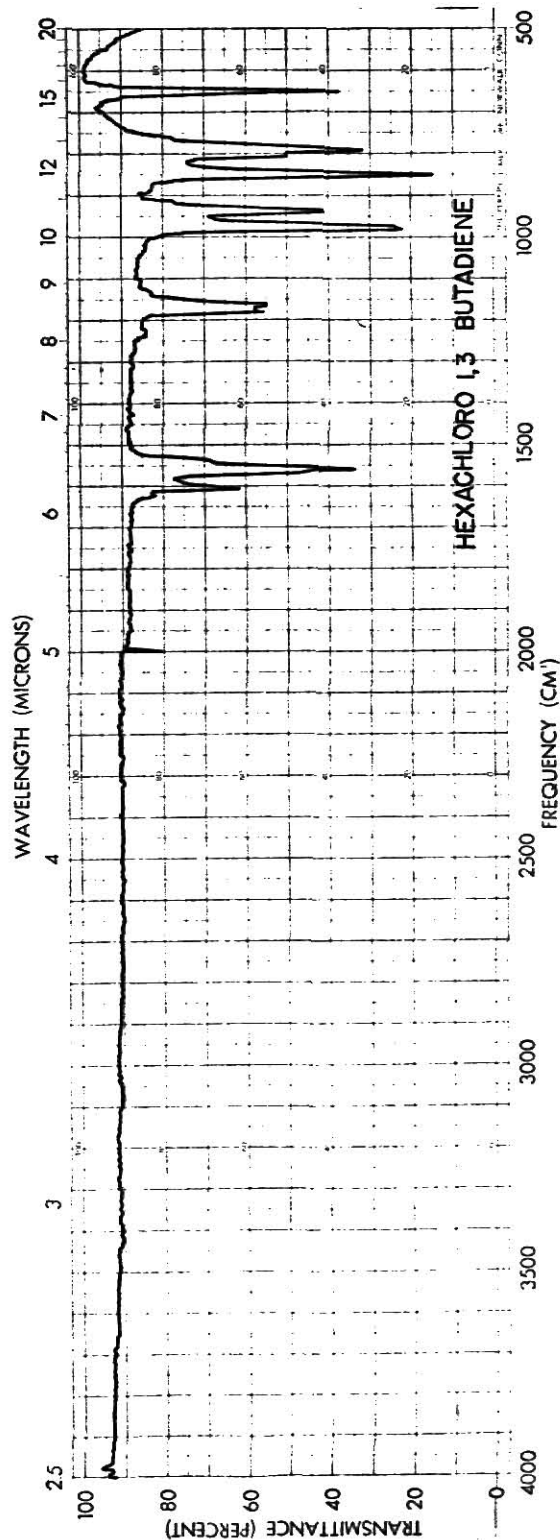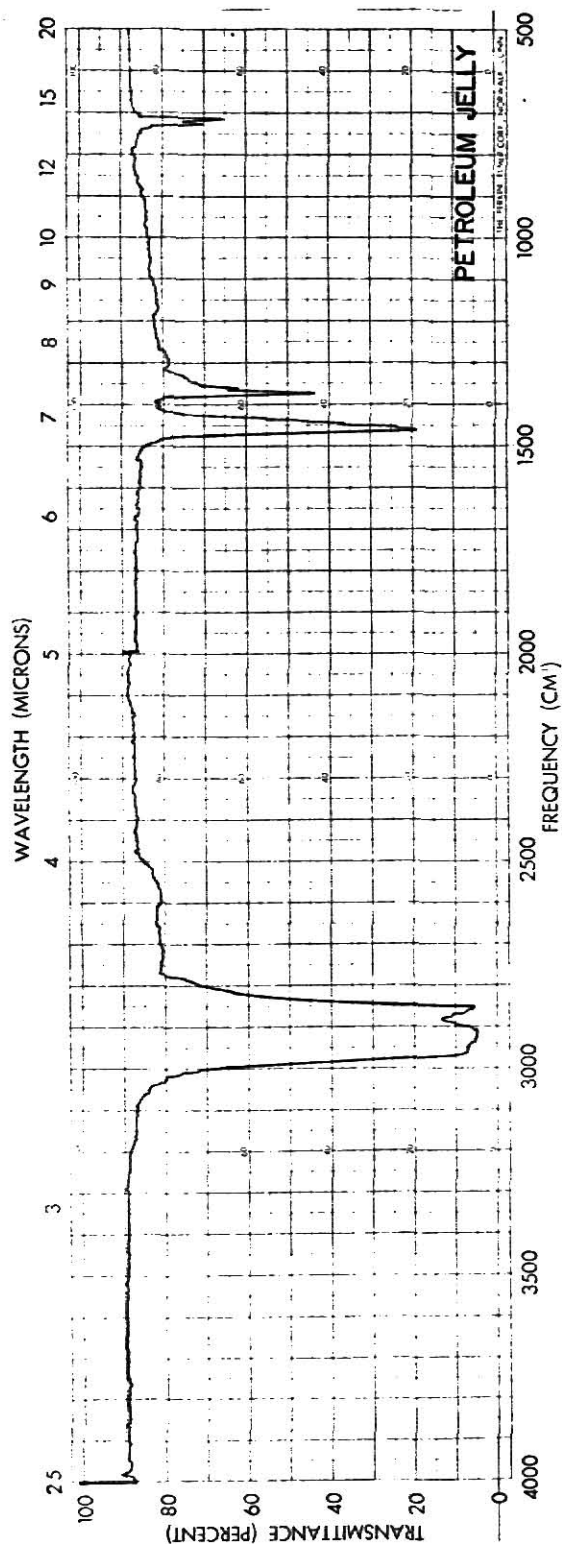
THIS IS THE BEST
COPY AVAILABLE

PETROLEUM JELLY

WAVELENGTH (MICRONS)

FREQUENCY (CM⁻¹)

TRANSMITTANCE (PERCENT)

HEXACHLORO 1,3 BUTADIENE

WAVELENGTH (MICRONS)

FREQUENCY (CM⁻¹)

TRANSMITTANCE (PERCENT)

Figure 21. The spectra of (1) glucose (G-1),
(2) maltose (G-2), (3) G-3, and (4) G-4.
The discontinuity in the spectrum at 2000
cm^{-1} is caused by changing the mulling
material from hexachloro 1,3 butadiene to
Vaseline.

WAVELENGTH (MICRONS)

G-1

G-2

G-3

G-4

TRANSMITTANCE (PERCENT)

FREQUENCY (CM⁻¹)
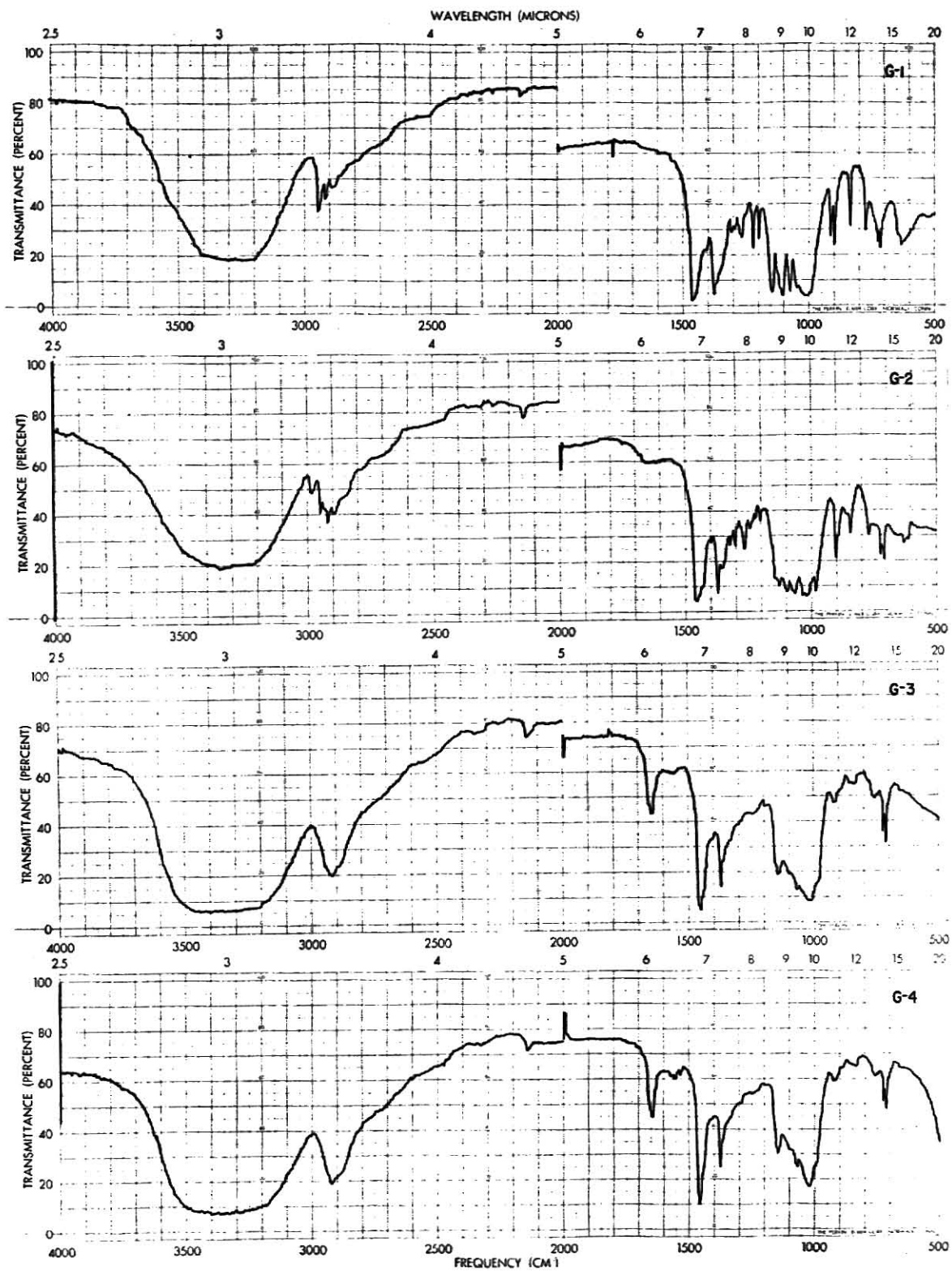
indicated in Figures 21-23, G-3 through G-12 have spectra different from G-1 and G-2 in this spectral region but they are not differentiable among themselves.

Thus, with the spectrometer used and the techniques used in this study, it would be possible to differentiate pure samples of G-1 and G-2. Any other sugar polymer could only be identified as "G-3 or greater".

Since one of the purposes of this study was to provide a spectroscopic technique for the identification of these sugar polymers, the discovery that they were, for the most part, indistinguishable at frequencies higher than 500 cm^{-1} presented an impasse of sorts. Apparently the frequency range covered excited modes of vibration involving end groups only while the rest of the interior glucose units of the polymeric chain remained relatively unperturbed. For this reason, G-3 through G-12 were very similar since they have the same end groups and differ only in the number of interior glucose units in the chain. Therefore, we reasoned, frequencies lower than 500 cm^{-1} might be expected to excite vibration modes involving the entire chain and thereby give rise to a characteristic spectrum for each species.

These lower frequencies pose problems in infrared spectroscopy because of the relatively small amounts of radiant power provided by standard infrared sources at long wavelengths. However laser Raman spectroscopy provides a powerful technique for routinely observing frequencies on the order of 100 cm^{-1} or less without the associated problems usually encountered using infrared spectroscopy in this spectral region.

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Figure 22. The polymers of glucose: (1) G-5,
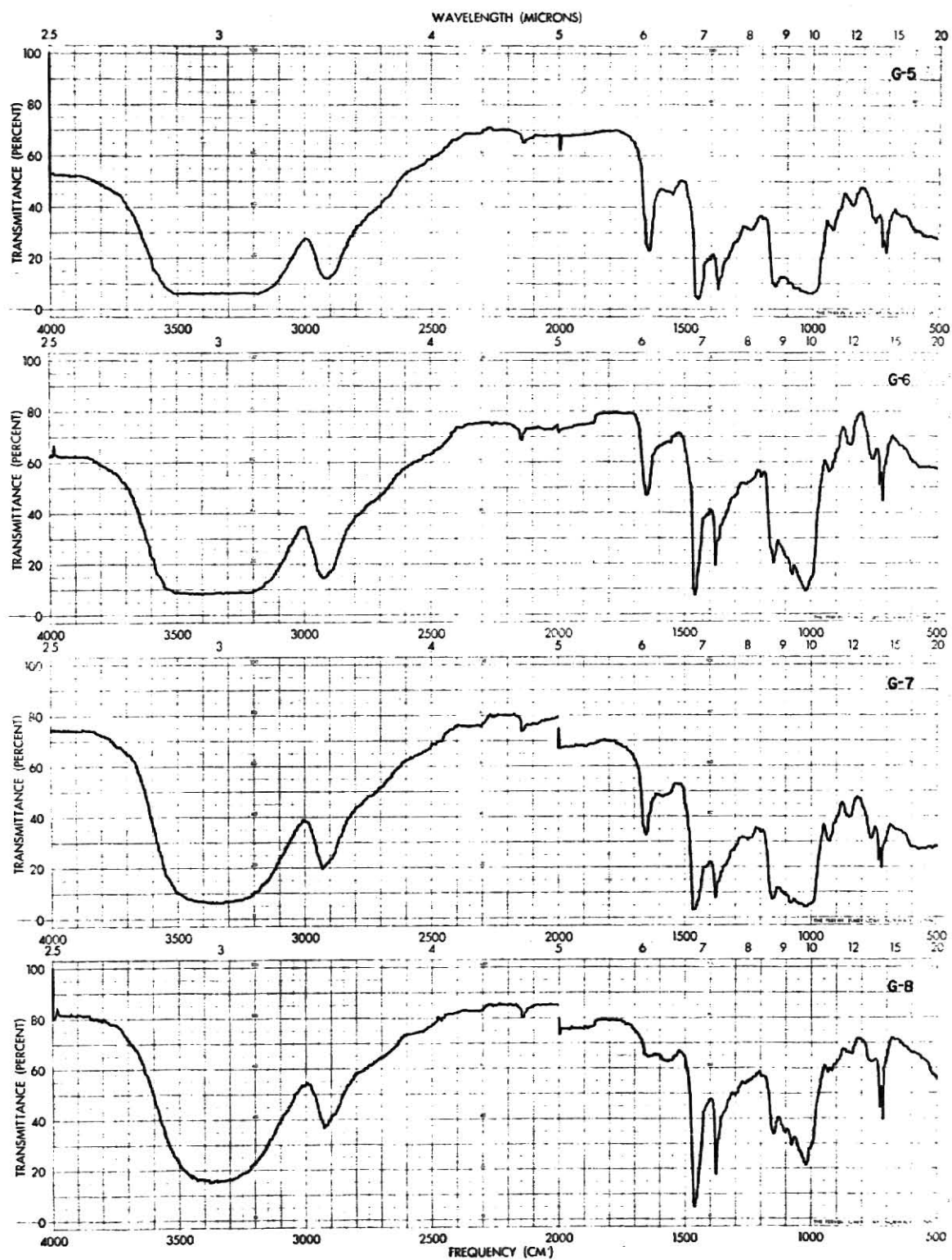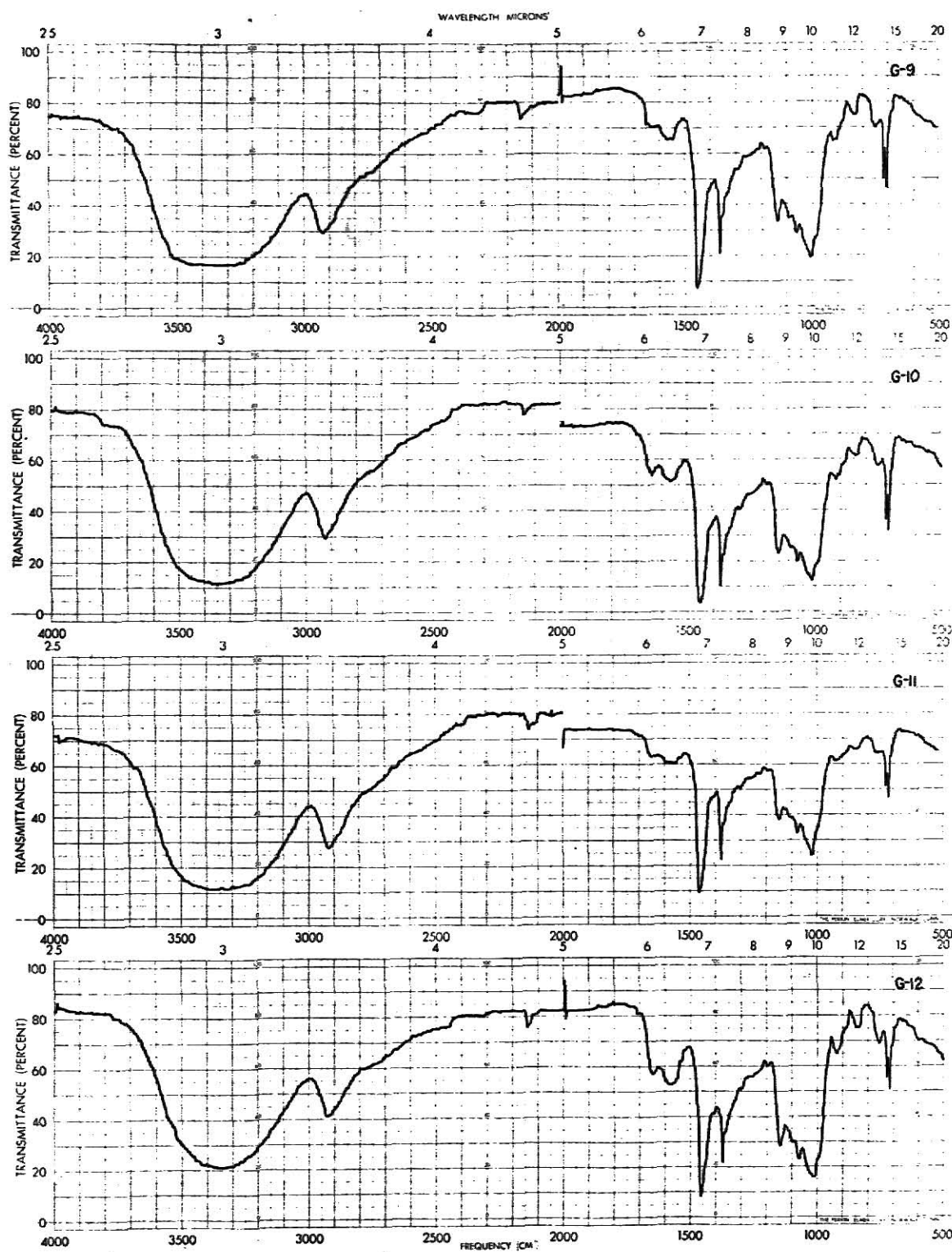(2) G-6, (3) G-7, and (4) G-8.

Figure 23. The polymers of glucose: (1) G-9,
(2) G-10, (3) G-11, (4) G-12.

The Raman spectra of the samples G-1 through G-12 were taken with the Raman assembly in Professor Hathaway's laboratory in the Department of Physics of Kansas State University. This assembly uses a Spex Model 1401 Double Spectrometer with an associated photodetector and counting circuit. The laser source is a Coherent Radiation Model 52 argon ion laser. The data were recorded at a scan rate of 50 cm^{-1} sec^{-1} with a time constant of two seconds and a slit width of 160 microns. This allows a resolution of ± 4 cm^{-1}. The data were plotted by a Mosely Autograf Model 2D-2 X-Y recorder.

All samples were prepared identically by forcing small amounts of sugar into 1mm ID Kimax capillary tubes with the aid of a small stiff wire. The samples were loosly tamped but not packed. The ends of the tubes were immediately sealed with wax.

The 514.5nm line of the argon ion laser was chosen for use in this study. The laser has a maximum continuous output of 750mW at this wavelength. This was more than enough power and, in most cases, the beam was attenuated by neutral density filters before it reached the sample.

The G-1 Raman spectrum in Figure 24 shows abundant structure from 200 cm^{-1} to 3600 cm^{-1}. Frequencies below 200 cm^{-1} are potentially very useful but the magnitude of the Rayleigh scattering, which arises from microscopic inhomogenieties of the dielectric constant of the sample that result from entropy changes and pressure waves in the crystals, prohibited starting the scan any closer than 100 cm^{-1} away from the frequency of the laser line. Even then, the Rayleigh scattering is appreciable until

one reaches 200 cm^{-1}.

The G-2 spectrum in Figure 24 shows a different low frequency spectrum from G-1. This is consistent with the earlier results obtained with infrared spectroscopy. However, starting at about 2200 cm^{-1} a new feature appears. A gradual rise in the background scattered radiation is apparent and detail that we expect to be present is obscured or obliterated. Only the strong complex of Raman bands around 2900 and 3300 cm^{-1} show through the rising background of noise. This background arises from fluorescence of the sample in the laser beam. Visual observation of the sample in the laser beam confirmed a definite red fluorescent glow at the point where the laser beam struck the sample. This phenomenon in G-2 (maltose) has been previously noted by Vasko et al.[27]

As far as the G-2 sample is concerned, the fluorescence at higher frequencies is of no practical significance since we are principally interested in the spectral region below 500 cm^{-1}. However, for G-3 and higher polymers, this fluorescence is present over the entire available spectrum and completely frustrates any attempts to obtain usable data. In the hope that a lower frequency laser line would not cause the samples to fluoresce, or at least cause it to be less intense, a Spectra Physics Model 125 helium neon laser with a wavelength of 632.8nm was tried. The fluorescence persisted.
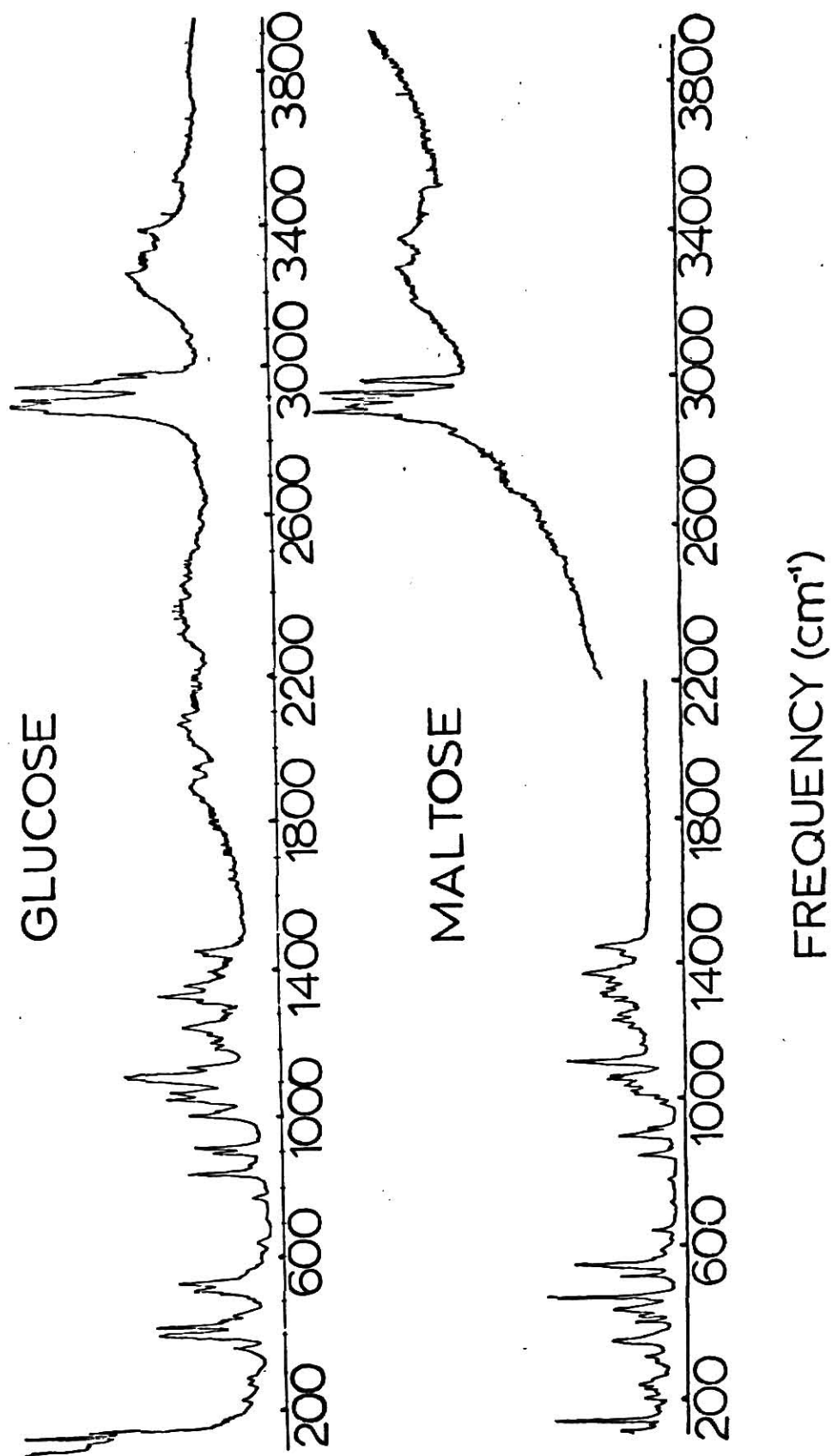
The Raman spectra reproduced in Figure 24 are the so-called "Stokes" spectra of the samples. The Stokes spectrum is recorded by scanning to progressively lower frequencies than the

exciting laser line. It is also possible to scan to progressively higher frequencies than the exciting laser line. The resulting Raman spectrum is the "Anti-Stokes" spectrum of the sample. One of the limitations of Anti-Stokes Raman spectroscopy is that scanning is limited to only a few hundred wavenumbers higher than the exciting laser line. An advantage, however, is that fluorescence of the sample is not observed.

We recorded the Anti-Stokes Raman spectra of the samples G-1 through G-12. Preliminary indications are that all of the samples show great similarities down to frequencies as low as 100 cm^{-1}.

On the basis of the results of our Stokes Raman spectroscopy and on the basis of our preliminary results obtained by using Anti-Stokes Raman spectroscopy, we conclude that Raman spectroscopy is not the answer to our search for a method of differentiation of the various glucose polymers.

Figure 24. The Raman spectra of (1) glucose and (2) maltose. The discontinuity in the maltose spectrum is a result of changing the chart recorder gain to compensate for rising background noise caused by sample fluorescence.

GLUCOSE

MALTOSE

FREQUENCY (cm⁻¹)

200 600 1000 1400 1800 2200 2600 3000 3400 3800

ACKNOWLEDGEMENTS

AN INFRARED STUDY OF WATER IN SEVERAL INORGANIC
CRYSTALLINE HYDRATES AND ORGANIC COMPOUNDS

by

ROBERT JULIEL BROCKMAN

B.S., Kansas State University, 1968

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AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

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Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1972

ABSTRACT: AN INFRARED STUDY OF WATER IN SEVERAL INORGANIC
CRYSTALLINE HYDRATES AND ORGANIC COMPOUNDS

In this study four inorganic crystalline hydrates were
examined by using infrared spectroscopic techniques. The hy-
drates were copper(II) sulfate pentahydrate, copper(II) chloride
dihydrate, cobalt(II) chloride hexahydrate, and calcium sulfate
dihydrate. We found that copper sulfate and calcium sulfate
had two distinct nonequivalent sites for the waters of hydration
in the crystal; this resulted in multiple fundamental water ab-
sorption bands. Cobalt chloride was found to have asymmetrical
water molecules in equivalent sites. Copper chloride water
molecules were found to be equivalent and symmetrical.

The effect of adding water to three organic solvents, ace-
tone, acetonitrile, and methanol, was studied. We found that
acetonitrile interacts only slightly with water, acetone inter-
acts with water to a greater extent than acetonitrile and meth-
anol interacts with water the most strongly of the three solvents.

Finally, water in agar and gelatin films was examined. We
found that the water in the films was more ordered than in liquid
water and that this ordering could be modified by the addition
of alkalai halides. The changes in the water bands in these films
in response to the addition of the alkalai halides to the films
resembles changes that occur in liquid water when the water's
temperature is changed. The fluoride ion caused the water in the
films to resemble pure water that had been cooled, while the
chloride, bromide and iodide ions causes the water in the films
to resemble pure water that had been heated.