THE INFRARED ABSORPTION SPECTRUM
OF FORMALDEHYDE VAPOR

DISSERTATION

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INTRODUCTION

The formaldehyde molecule has been the subject of a number of spectroscopic investigations. In particular excellent data have been obtained in the microwave and ultraviolet regions. Rather extensive work was done on the infrared absorption spectrum of formaldehyde prior to 1940. Since that date the design of infrared spectrometers has improved tremendously and today the same spectra can be recorded with significantly better resolution.

The Coriolis resonance interaction was first recognized in formaldehyde. A theoretical treatment of the problem was effected but the spectra obtained for the bands in question were not sufficiently resolved to permit an exact testing of the theory. With the high resolution attainable today, it is possible to resolve the rotational structure of these bands.

The six fundamental bands in the formaldehyde spectrum were identified in the early infrared investigations. The assignment of two of the bands has been questioned by a number of investigators, but the problem is as yet unresolved. A careful study of the rotational structure of the two bands should afford an answer to the question.

Finally the ν_3 band has previously been seen only under low resolution. This band falls in a region where water vapor absorbs intensely. The near infrared vacuum spectrometer used in this investigation permits recording the ν_3 spectrum without interference from atmospheric absorptions.

The purpose of this investigation is to record the absorption spectrum of formaldehyde vapor for the region extending from 3 to 10 microns under high resolution, to study the ν_3 band without interference from atmospheric absorptions, and to carry out an analysis of the bands coupled by rotational resonance interactions.

HISTORY

The infrared absorption spectrum of H_2CO was first investigated by Salant and West¹ using a prism spectrometer. Spectral bands were reported at 3.5 microns, 1.8 microns, 1.4 microns, and 1.25 microns in the order of decreasing intensities. Patty and Nielsen² confirmed the existence of these bands and reported the existence of an additional band at 4.8 microns. In addition, the 3.5 and 4.8 micron regions were examined under high dispersion using a grating instrument and the structure was partially resolved. The 3.5 micron region was found to consist of three badly overlapping bands two of the parallel and one of the perpendicular type. The 4.8 micron region was found to be a single parallel type band.

Two years later Nielsen³ repeated these measurements under better experimental conditions and extended his observations to 11.0 microns. Additional bands were reported at 5.7 microns, 6.7 microns, 7.5 microns, 8.6 microns, and 9.6 microns. All of these bands were measured with a grating instrument and all except that at 6.7 microns were at least partially resolved, although the measurements of the 9.6 micron band were incomplete. The intense region of absorption at 5.7 microns was found to be a single band of the parallel type. The 6.7 micron region was also found to be a parallel type band, although only the envelope could be recorded due to interference from the intense water vapor band at 6.3 microns.

The region extending from 7.5 microns to 10.0 microns was later remeasured by Ebers and Nielsen⁴. Two bands at 7.8 microns and 8.6

microns were observed in place of the three reported earlier. The spurious band previously observed at 9.6 microns was attributed to impurities. The two bands were found to be of the perpendicular type and exhibited an anomalous spacing between principal rotational lines that was accounted for on the basis of an interaction between rotation and the two slightly anisotropic oscillations.

A study of the infrared absorption spectrum of D_2CO from 2.0 microns to 13.0 microns was later conducted by Ebers and Nielsen⁵. Seven absorption bands were observed including all six fundamentals. The fundamental vibrational frequencies of both the H_2CO and D_2CO molecules were then identified with considerable certainty through the use of isotopic product relationships.

An excellent study of the ultraviolet absorption spectrum of H_2CO was made by Dieke and Kistiakowsky⁶. The structure of the ultraviolet bands was resolved and values of the rotational constant, a , b , and c , were reported for both upper and lower state for four of these. These values were determined by using the theory of the symmetric top molecule applied to lines relatively far removed from the band centers.

A recent microwave study of the H_2CO molecule by Lawrance and Strandberg⁷ rather spectacularly confirmed the ground state a , b , and c values as reported by Dieke and Kistiakowsky. The microwave values were obtained by fitting the observed pure rotational lines with asymmetric top energy levels. In addition, the effects of centrifugal distortion were accounted for and so it would appear that the listed values of a , b , and c are quite accurate.

Recently Davidson, Stoicheff, and Bernstein⁸ reported on the infrared and Raman spectrum of HDCO. All six fundamentals were observed in the infrared and four were observed in the Raman spectrum of the vapor. These data were recorded by using a prism spectrometer and consequently the resolution of the bands was incomplete.

EXPERIMENT

A. Apparatus

At room temperature formaldehyde polymerizes readily and condenses as solid paraformaldehyde on cool surfaces. The polymerization and condensation can be retarded through use of an absorption cell that can be heated. The reversible reaction is $(\text{H}_2\text{CO})_x \rightleftharpoons x(\text{H}_2\text{CO})$, and the equilibrium point is displaced in favor of the monomeric vapor with increase in temperature.

Formaldehyde can also be obtained as a liquid monomer. The solid polymer is sublimed over to a cold trap held at -78.5 degrees centigrade where the liquid is collected. At this temperature the liquid has a vapor pressure of approximately 2 cms. of Hg.

Both of the above mentioned sources of the vapor have been utilized for absorption studies with identical results. The first method was used here, since it permits considerable control of the pressure of the sample in the absorption cell.

Two absorption cells of somewhat different design were used. A diagram of the first cell and its furnace is presented in Figure 1. The cell body was made from a pyrex cylinder 2.5" in diameter and 9" in length. Rock salt windows were cemented to the cell body with glyptal. Several thin layers of glyptal were applied and each was baked for several hours at 125 degrees centigrade.

The furnace was made from a brass cylinder fitted with threaded rings that could be turned in to exert a compressive force on the cell and windows. The rings were fitted with springs, so that the windows

would still be supported when the furnace body lengthened upon heating.

The brass cylinder was coated with a layer of asbestos paper upon which a coil of nichrome wire was wound. The heating coil was wound so that the windows would be heated slightly more than the remainder of the cell. Finally, a second layer of asbestos was applied over the nichrome wire.

The second cell which is illustrated in Figure 2 was designed for use in an evacuated chamber. The cell body was made of brass upon which the heating coils were wound as described above. Neoprene gaskets lightly coated with silicone vacuum grease were placed between the rock salt windows and the cell body. The windows were pressed tightly against the gaskets by means of threaded rings.

Although the design of the first cell made it unsuitable for use in a vacuum chamber, sufficient spectra were recorded by using it to determine that the brass cell did not introduce any detectable impurities.

In operation the paraformaldehyde was placed directly in the cell. The cell was then thoroughly evacuated, sealed off, and finally heated to the desired temperature. The vapor pressure of the formaldehyde was varied from approximately one to six or seven centimeters of Hg. pressure where the strength of the band under consideration determined the pressure used.

Two prism-grating high dispersion spectrometers were used to obtain the spectra. Figure 3 is a diagram of the optics of the first instrument⁹. The grating used in this spectrometer was ruled with 4500 lines

per inch and a thermocouple was used as the detector.

The spectrometer bed was fitted with a steel tank, so that the instrument could be evacuated. In addition, the external optics as well as the absorption cell were housed in a source tank that could be evacuated. Consequently, the entire optical path except for that portion occupied by the absorption cell was a vacuum path and interference from atmospheric absorptions was not a problem. A diagram of the source tank is presented in Figure 4.

This spectrometer was used to obtain the trace of the spectral bands in the 5.7, 6.7, and 7.5 to 10 micron regions.

The spectral bands in the 3 to 4 micron region were recorded with the second instrument¹⁰. The internal optical arrangement of this spectrometer was very similar to that of the first instrument differing only in the design of the foreprism section. This spectrometer was equipped with a grating ruled with 7200 lines per inch and a lead telluride cell as detecting element.

Unfortunately, it was not possible to evacuate the instrument and, consequently, it was necessary to run a background of the atmospheric absorption lines in the region of interest. Even in view of this difficulty, the high sensitivity of the PbTe detector in the 3 to 4 micron region made it desirable to use this spectrometer.

B. The Spectra

The spectra were obtained in the conventional manner. Frequencies were determined by linear interpolation between marks placed on the chart at intervals of five minutes of arc as determined by reading the grating circle. Errors in the marker positions are estimated to be somewhat less than five seconds of arc. The slight eccentricity in the motion of the grating produced by the last worm gear in the drive introduces a negligible error, since the interval between two adjacent markers covers but a small fraction of the period of the eccentricity.

In both spectrometers which were used, the grating circle and grating are in fixed positions with respect to each other and rotate as a unit. Since the axis of rotation of the grating does not precisely coincide with the center of the grating circle, the measured angle is not the true grating angle. The difference between the true and measured angle plotted as a function of the measured angle is a sine curve with a period of 2π . In order to minimize the error introduced by this effect, the central image was fixed at an angle such that the deviation between true and observed angle for the central image position was approximately the same as for the angles at which the spectra were recorded. In addition, the central image position was such that the sine function was a slowly varying function over the angular region used in recording the spectra.

A number of runs were taken for each band and the best two or three of these were used in the frequency calculations. The grating constant was obtained from spectra of the carbon monoxide first overtone

in the second order. The usual grating equation $n\lambda = k/\sin(\theta - \theta_0)$ was used where n is the order, k is the grating constant, θ the measured angle and θ_0 is the central image angle. The carbon monoxide line frequencies used were those reported by Benedict¹⁴. The marker position and grating circle eccentricity errors in calibration runs introduce an estimated error of 0.01 cm^{-1} in the reported line frequencies.

The line frequencies reported for the three to four micron region were reduced to vacuum frequencies by using the equations of Downie¹⁵. In addition, a temperature correction was applied, since the position of the central image changed slightly with change in temperature for the non-evacuatable instrument. This correction was derived by assuming that the spectral lines observed shifted with the central image in a 1 to 1 ratio. The temperature was noted at five minute intervals when the spectra were recorded. The correction curve was based on a large number of records of central image angle at a number of different temperatures.

It was not necessary to apply a temperature correction to the frequencies of the lines recorded with the vacuum instrument.

The absolute error in reported line frequencies is estimated to be 0.04 cm^{-1} in the 7.5 to 10 micron region, 0.06 cm^{-1} in the 5.7 and 6.7 micron regions, and 0.09 cm^{-1} in the 3 to 4 micron region. The relative error in each of these regions is 0.01 cm^{-1} less than the above values.

No attempt was made to determine the absolute intensities of the spectral lines. It was necessary to change the position of the fore-prism a number of times while recording a particular spectral band and

there was no convenient method for quickly determining a zero of absorption.

The relative intensities of the lines as illustrated in the photographs of the spectra are approximately correct, although it was sometimes necessary to scale in certain portions of a band. The scaling was necessary, since it was difficult to hold the sample pressure at a constant value and, further, since the pressure was frequently varied intentionally to bring out weak lines.

THEORY

A. Vibrational Problem

Formaldehyde is a planar molecule of point group C_{2v} , that is, a molecule with a two-fold axis of symmetry C_2 and two planes of symmetry σ_v through this axis.

A second possible configuration, a pyramidal form with a single plane of symmetry is excluded by the observation of a three to one intensity alternation in the rotational structure of the infrared and ultraviolet bands.

The normal modes of vibration of the molecule are illustrated in Figure 5 where the assignment of fundamentals follows the notation of Herzberg. Clearly the normal vibrations ν_1 , ν_2 , and ν_3 are symmetric with respect to both planes of symmetry, ν_4 and ν_5 are symmetric with respect to the plane of symmetry $\sigma(yz)$, the plane of the molecule, and antisymmetric with respect to $\sigma(xz)$, and ν_6 is antisymmetric with respect to $\sigma(yz)$ and symmetric with respect to $\sigma(xz)$.

Although the symmetry properties of the fundamental vibrations are readily determined by inspection, the situation is not so obvious in the case of overtone and combination bands. Consequently, it is convenient to use the vibrational symmetry species notation appropriate to the point group.

The point group C_{2v} has two necessary elements of symmetry, and there are four possible symmetry types designated as ++, +-, -+, and --, where the first sign refers to the plane of symmetry $\sigma(yz)$ and the second to the plane $\sigma(xz)$. These symmetry types are in turn designated

as A_1 , A_2 , B_1 , and B_2 respectively.

The symmetry species of a combination or overtone band is obtained by multiplying the symmetry types of the component states term by term. Thus for example, $2\nu_3'$ is of type A_1 while $\nu_2' + \nu_5'$ is B_1 .

B. Rotational Problem

Formaldehyde is an asymmetric top molecule, but the degree of asymmetry is small and consequently the gross features of the rotational spectra resemble those of a symmetric molecule. For this reason, it is convenient to begin with a brief discussion of symmetric top theory.

The rotational term for a rigid, symmetric top is

$$F(J,K) = a_v J(J+1) + (a_v - 1/2(b_v + c_v))K^2$$

$$\text{where } a_v = \frac{h}{8\pi^2 c I_{a_v}}, \quad b_v = \frac{h}{8\pi^2 c I_{b_v}}, \quad c_v = \frac{h}{8\pi^2 c I_{c_v}}.$$

J is the quantum number associated with the total angular momentum, K is the quantum number associated with the projection of the total angular momentum along the top axis, and I_{a_v} , I_{b_v} , I_{c_v} are the principal moments of inertia for the v vibrational state.

For an asymmetric molecule, the principal moments of inertia are usually defined, so that $I_a < I_b < I_c$. In this case I_a is the moment of inertia about the C-O axis, I_b is the moment of inertia about the axis in the plane of the molecule and perpendicular to the top axis, and I_c is the moment of inertia about the axis perpendicular to the plane of the molecule and to the symmetry axis. It is approximately true that

$$I_{b_v} = I_{c_v}.$$

In the equilibrium state $I_{a_e} = I_{b_e} + I_{c_e}$ since here the molecule is strictly planar. When the effects of vibration and rotation are introduced, it is necessary to express the rotational constants in the form

$$a_v = a_e - \sum_i \alpha_i^a (v_i + d_i/2)$$

where the α_i^a are small constants, v_i are vibrational quantum numbers, and the d_i are positive integers that depend on the degeneracy of the vibrational state.

This correction is necessary since $(r^2)_{\text{avg.}} \neq (r_e^2)$, the potential function for the vibrating atoms is not harmonic, and the vibrating atoms experience a coriolis force because of the rotation of the molecule as a whole.

It should be noted that values of I_{a_v} , etc. determined from a_v , etc. are not simply average values of the moments of inertia. This follows as a consequence of the fact that $(\frac{1}{r})_{\text{avg.}} \neq \frac{1}{(r)_{\text{avg.}}}$. Therefore, the simple relation between the equilibrium moments of inertia would not hold for those determined spectroscopically even if the influence of vibration and rotation was neglected.

An additional correction to account for centrifugal distortion will not be included, since the effect was not observed spectroscopically.

The selection rules for a symmetric top molecule are

$$\begin{array}{lll} \Delta K = 0, \Delta J = 0, \pm 1 & \text{if } K \neq 0 & J \geq K \\ \Delta K = 0, \Delta J = \pm 1 & \text{if } K = 0 & \end{array}$$

where the oscillating electric moment is along the symmetry axis, and

$$\Delta K = \pm 1, \Delta J = 0, \pm 1 \quad J \geq K$$

where the oscillating moment is perpendicular to the symmetry axis. These transitions give rise to two distinct types of bands designated as parallel and perpendicular bands.

In a parallel band transitions occur only between levels with the same K value. For a particular value of K , since $\Delta J = 0, \pm 1$, there results a sub-band with P, Q, and R branches. The complete parallel band consists of a superposition of a number of such sub-bands corresponding to the various K values that are important at the temperature of observation. So long as the difference between the upper and lower state a and $1/2(b+c)$ values is small, the sub-bands will very nearly coincide.

A perpendicular band where $\Delta K = \pm 1$ also consists of a number of sub-bands. In this case, however, the sub-bands do not even approximately coincide and a rather complicated band results. In general, if $a \gg 1/2(b+c)$ the individual Q branches stand out rather prominently against a background of weaker lines that are due to the P and R lines of the various sub-bands.

It should be noted that there is, with increasing K , and increasing number of lines missing near the centers of the sub-bands. The lines are absent because of the requirement $J \geq K$. Particularly in the case of parallel bands, the missing lines permit the various sub-bands to be identified readily if the rotational structure is sufficiently resolved.

Since the formaldehyde molecule is symmetric with respect to a rotation by 180 degrees about the symmetry axis, the rotational eigenfunctions can at most change sign as a result of the rotation. For the

ground-state levels with even K are symmetric with respect to the rotation, while those with odd K are antisymmetric.

The situation that exists here is analogous with that which exists for the hydrogen atom. In order that the total eigenfunction shall be antisymmetric as is required by the statistics of the identical nuclei, it is necessary to multiply the eigenfunction for each energy state by an appropriate spin eigenfunction.

As a consequence ground state terms with odd K have three times the statistical weight of states with even K . This leads to a three to one intensity alternation between adjacent sub-bands for perpendicular and for parallel bands. Sub-bands originating from even K states are weak or para bands while those originating from odd K states are strong or ortho bands.

Although many of the features of the rotational structure of the absorption bands can be explained on the basis of the symmetric top formulation, it is necessary to consider the effects of asymmetry.

The rotational term for a rigid, asymmetric top is

$$F(J) = \frac{(a+c)}{2}J(J+1) + \frac{(a-c)}{2}E_J^J(\kappa) \quad 11$$

where $\kappa = \frac{2b - a - c}{a - c}$, the asymmetry parameter.

$E_J^J(\kappa)$ is a complicated quantity that depends on a , b , c , and J and for a given J assumes $2J+1$ different values.

An entirely equivalent expression for the rotational term is

$$F(J) = 1/2(b+c)J(J+1) + (a-1/2(b+c))W_J^J \quad 12$$

W_r^J and E_r^J are closely related terms that produce an equivalent effect.

The first formulation is particularly useful for computation purposes, since elaborate tables of E_r^J are available¹³. The second formulation differs from the symmetric top rotational term only in the substitution of W_r^J for K^2 . For this reason, it is somewhat more straightforward to use this equation to illustrate the effects of asymmetry.

Each of the energy levels of a symmetric top except for $K = 0$ is doubly degenerate since $K = \pm$ does not change the magnitude of the energy term. When the influence of anharmonicity is taken into account, the degeneracy is removed. For each value of J there are $2J + 1$ levels given by the $2J + 1$ values of E_r^J . These correspond to the permitted values of K for each J , that is, to $K = 0, \pm 1, \dots, \pm J$.

Although the introduction of asymmetry removes the K degeneracy, the degree of splitting of the degenerate levels depends upon the asymmetry parameter κ . In the case of a prolate molecule, κ can vary from -1 for the completely symmetric case to 0 for the most asymmetric case.

For a given value of κ the splitting increases with increasing J and decreasing K . This last statement is somewhat ambiguous since K is not a valid quantum number for an asymmetric molecule. The K notation is retained only to show the relation between the symmetric and asymmetric levels.

Formaldehyde is very nearly symmetric. In the ground vibrational state $\kappa = -0.961$ as determined from microwave studies. Splitting of the degenerate levels is negligible for values of K equal to or greater

than three even for high J . For values of K less than three the splitting is important and corresponding regions in the spectra must be treated by using the asymmetric formulation.

The rotational symmetry of an asymmetric molecule is described in terms of the + or - behavior of the rotational eigenfunction with respect to rotations by 180 degrees about the three principal axis. These rotations are denoted by the operators C_2^a , C_2^b , and C_2^c . Knowledge of behavior with respect to any two of them gives the behavior with respect to the third, since there are but two necessary elements of symmetry. C_2^c and C_2^a are customarily chosen to represent the symmetry species. There are four species described by ++, +-, -+, -- where the first sign refers to behavior with respect to C_2^c and the second to C_2^a .

When the symmetry axis coincides with the axis of least moment of inertia as is the case for formaldehyde, the species have symmetry classification A or B for ++, -+ and +-, -- respectively. Pairs of levels that correspond to a particular value of K in the symmetric case have the same symmetry and, therefore, the ortho-para considerations mentioned above are unchanged.

In addition to the usual rotational selection rules $\Delta J = 0, \pm 1$, there are rules related to the direction of change of the dipole moment during vibration. If the alternating moment lies along the axis of least moment of inertia, the permitted transitions are ++, -+, and +-, --. This case corresponds to $\Delta K = 0$ for the symmetric top.

If the alternating moment lies along the axis of intermediate moment of inertia, the permitted transitions are ++, --, and +-, -+.

If the alternating moment lies along the axis of greatest moment of inertia, they are ++, +-, and +-, ---. The last two correspond to $\Delta K = \pm 1$ for the symmetric top.

These three sets of selection rules give rise to bands designated as type A, B, and C bands respectively. Although types B and C are quite similar for a slightly asymmetric molecule, identification of the rotational lines in the regions of greatest effective asymmetry permits an unambiguous assignment of fundamental bands.

C. Resonance Interactions

It is frequently true that two vibrations or two combinations of vibrations have frequencies that are very nearly the same. The inclusion of the effects of anharmonicity in the potential energy expression for the molecule then gives rise to terms that produce a vibrational interaction or resonance.

Terms cubic in the coordinates in the first order Hamiltonian introduce a second order term¹⁶ with the denominator $(\lambda_s'' + \lambda_{s'}'' - \lambda_{s''}''')$ where the λ_s'' are directly proportional to the frequencies ν_s . When the combination frequency $\lambda_s'' + \lambda_{s'}''$ is nearly equal to $\lambda_{s''}'''$ resonance occurs. Additional terms from the second order Hamiltonian also introduce resonance denominators of comparable form.

The mathematical treatment of a vibrational resonance problem is carried out by using degenerate perturbation methods and is quite complicated. The general effects of the interaction can, however, be discussed without reference to the development.

The two accidentally degenerate vibrational levels repel each other. This results in a displacement of the observed frequencies with respect to their positions in the absence of interaction. In addition, the rotational constants characteristic of the energy states involved are changed slightly because of the interaction.

The intensities of the spectral bands are also influenced. In general combination and overtone bands are much weaker than the fundamentals. Resonance between a combination band and a fundamental results in a mixing of the eigenfunctions of the two states and a consequent increase in the intensity of the combination band. In effect the normally weak band borrows intensity from the strong band.

A second type of resonance known as rotational or Coriolis resonance gives rise to rather striking effects in the formaldehyde spectrum.

This interaction can be illustrated classically by consideration of the effects of the rotational motion of the molecule on the vibrational motion. Each atom experiences a Coriolis force which is directed at right angles to the direction of its vibratory motion. In special cases the Coriolis forces experienced by the vibrating atoms in a particular normal mode tend to excite a second normal mode of oscillation.

In general the degree of excitation is small, but when the two normal frequencies are close to one another, the coupling is strong. In this case the atoms move in ellipses and contribute a component of internal angular momentum.

The first order Hamiltonian¹⁶ contains terms of the form $p_\alpha P_\alpha / I_\alpha$

where P_α is an operator corresponding to the component of the total angular momentum directed along the principal axis of inertia and p_α is the component of internal angular momentum along the same axis. The internal angular momentum may be expressed as

$$p_\alpha = \mathcal{J}_{ss'} \left(\left(\frac{\lambda_{s'}}{\lambda_s} \right)^{1/4} q_s p_{s'} - \left(\frac{\lambda_s}{\lambda_{s'}} \right)^{1/4} q_{s'} p_s \right)$$

where p_s is the momentum associated with the vibrational coordinate. q_s and $\mathcal{J}_{ss'}$ is the Coriolis coupling coefficient which depends in an involved manner on the normal coordinates associated with the interacting vibrations.

The Coriolis operator $p_\alpha P_\alpha / I_\alpha$ introduces a second order term with the denominator $(\lambda_s^{1/2} - \lambda_{s'}^{1/2})$. When the two frequencies are nearly the same, this term becomes large, and it is necessary to treat the problem using degenerate perturbation methods.

Coriolis type resonance was first identified in the two fundamental bands ν_5 and ν_6 of formaldehyde vapor by Nielsen⁴. These vibrations are perpendicular to the symmetry axis of the molecule, the first lying in the plane of the molecule and the second perpendicular to it. Since they are separated by only approximately 80 wavenumbers, the interaction is very strong.

The theory of Nielsen¹⁷ gives for the energy terms

$$F = \frac{\nu_5 + \nu_6}{2} + \frac{1}{2} (b+c) J(J+1) + \left(a - \frac{1}{2} (b+c) \right) W_T^J$$

for the ground state and

$$F = (\nu_5 + \nu_6) + \frac{1}{2}(b+c)J(J+1) + (a - \frac{1}{2}(b+c))W_r^J + aJ^2 + (a - \frac{1}{2}(b+c)) \\ \pm \left(\frac{\nu_5 - \nu_6}{2}\right)^2 + 4a^2 J^2 W_r^J$$

for the upper state. Here J is the coriolis coupling coefficient and the plus sign is taken with ν_5 and the minus with ν_6 .

A general picture of the structure of the interacting bands may be obtained if it is assumed that the rotational constants are the same in the upper and lower states and that the molecule is symmetric and that W_r^J is replaced by K^2 . The most prominent feature of the bands is formed by the Q branches that stand out sharply against a background of weaker lines which make up the P and R branches of the various sub-bands.

If the selection rules $\Delta J = 0, \Delta K = \pm 1$ are used with the above energy terms, there results

$$\nu_Q = \left(\frac{\nu_5 + \nu_6}{2}\right) + 2K(a - \frac{1}{2}(b+c)) + aJ^2 + (a - \frac{1}{2}(b+c)) \\ \pm \left(\left(\frac{\nu_5 - \nu_6}{2}\right)^2 + 4a^2 J^2 (K \pm 1)^2\right)^{1/2}.$$

When the values of K, K = 0, ± 1 , ---- are substituted, the frequencies for the Q branches are obtained.

When $\left(\frac{\nu_5 - \nu_6}{2}\right)^2$ is large with respect to $4a^2 J^2 (K \pm 1)^2$, the spacing between the lines approaches the normal value. As K increases the spacing approaches $2(a - \frac{1}{2}(b+c)) \pm 2aJ^2$. The lines in the region of the bands which overlap each other are crowded together, while those in the extremities are pushed apart. The P and R branch structure associated with the sub-bands is not altered to an appreciable extent. The individual sub-bands shift as is indicated by the Q branch positioning

but there is no evidence for anomalous spacing for lines within a sub-band.

According to the selection rule of Teller and Tiza¹⁸ the intensities of the ν_5 lines for $\Delta K = -1$ are enhanced at the expense of these for $\Delta K = +1$ while the converse is true for ν_6 . As a consequence, the lines in the overlapping regions of the bands are expected to be somewhat more intense than those in the extremities.

There is also a Coriolis interaction between the ν_3 and ν_5 fundamentals. The ν_3 vibration produces an oscillating moment parallel to the symmetry axis and ν_5 an oscillating moment perpendicular to the axis and in the plane of the molecule.

Quantum mechanically this case is very difficult to treat, and it has not been solved in detail. A partial development of a somewhat similar case has been carried out by Nielsen¹⁹ for the pyramidal XY_3 molecule.

Since ν_3 and ν_5 are separated by 250 cm^{-1} , the interaction is not so strong as is that between ν_5 and ν_6 . The effects of the latter resonance on the ν_5 band effectively hide those due to the former resonance. The situation is quite different for the ν_3 band where definite deviations from the structure of a type A band for a slightly asymmetric molecule are observed.

Classically ν_3 and ν_5 tend to excite each other through coriolis interaction only for rotation of the molecule about the axis of largest moment of inertia. Consequently, when $J = K$ in the upper state term, the molecule rotates about the symmetry axis and the interaction should

be very slight. Corresponding lines in the P, Q, And R branches of the ν_3 band should be displaced but little from their normal positions.

By analogy with the development for the XY_3 molecule, the interaction for $J \neq K$ is expected to cause the rotational lines in the various sub-bands to shift from their normal positions, so that partial resolution of the sub-bands is possible. The displacement of the lines is expected to be greatest when $J \gg K$ or when the tumbling motion of the molecule is most pronounced.

ANALYSIS

A. The 3 to 4 Micron Region

The three to four micron region is one of intense absorption (Figure 19). The complicated nature of the spectrum indicates that a number of badly overlapping bands are present. Figures 6 to 9 illustrate the absorption pattern. In order to resolve clearly the weak lines at either end of the spectrum higher sample pressures were used than in the central portion. In the figures, sufficient overlap is shown to permit a determination of relative intensities for lines in the several regions.

Line frequencies were obtained ranging from approximately 2500 to 3200 cm^{-1} . The two fundamentals ν_1 and ν_4 fall in this region and, in addition, five overtone and combination bands are predicted to fall here. The prediction is based on a calculation of band centers carried out by neglecting the influence of anharmonicity. Two of the seven possible bands have been definitely identified and a third tentatively identified.

The fundamental band ν_4 centered at 2843.41 cm^{-1} is the most prominent feature of the absorption pattern. This band, which is of type B, is badly hidden by overlapping bands on the low frequency side, but the Q branch structure and the associated R branch structure, stands out clearly on the high frequency side.

A number of lines in each of the branches R_{R_3} , R_{R_4} , R_{R_5} , and R_{R_6} was identified. Sub-band centers and upper state $\frac{1}{2}(b'+c')$ values were

then calculated using the symmetric top formulation.

The expression

$$R_R(J) = \nu_0^{\text{sub}} + (b' + c') + \left(\frac{3(b' + c')}{2} - \frac{(b'' + c'')}{2} \right) J + \frac{(b' - b'' + c' - c'')}{2} J^2$$

was used where the omitted term $((a' - \frac{1}{2}(b' + c') - (a'' - \frac{1}{2}(b'' + c''))K^2$ was considered to be negligibly small. Since it was not possible to find the weak lines in the R_{P_3} , R_{P_4} , R_{P_5} , and R_{P_6} branches or lines in the P_{P_3} , P_{P_4} , P_{P_5} , and P_{P_6} branches, the usual combination and difference relations could not be used. The ground state values of the rotational constants used in these calculations were those determined from microwave data by Lawrance and Strandberg⁷ and are listed in Table 1.

The calculated ν_0^{sub} values were then used with the equation

$$\nu_0^{\text{sub}} = \nu_0 + (a' - \frac{1}{2}(b' + c')) \pm 2(a' - \frac{1}{2}(b' + c'))K + ((a' - \frac{1}{2}(b' + c')) - (a'' - \frac{1}{2}(b'' + c''))K^2$$

to determine ν_0 and a' . In the above equation, the plus sign applies to $\Delta K = +1$ and the minus sign to $\Delta K = -1$ transitions.

An attempt was then made to use the constants determined from the symmetric data with the asymmetric terms to calculate the positions of the lines in the sub-bands corresponding to $K'' = 2, 1$, and 0 . Values of b' and c' were calculated from $\frac{1}{2}(b' + c')$ where a planar form for the molecule was assumed. This attempt was not successful since the sub-bands in question are badly confused by overlapping lines and since the asymmetric terms are very sensitive to small changes in the rotational

constants. The values of the constants determined in this partial analysis are listed in Table 1. The errors listed are averages of the absolute values of the deviations of the reported value of the constant from the values calculated from the frequencies of lines in the several sub-bands, as indicated above.

A second somewhat weaker type B band, that is believed to be $\nu_2 + \nu_5$, is located on the high frequency side of ν_4 . This band overlaps ν_4 , so that again only R_R and R_Q lines could be identified.

A type A band identified as $2\nu_3$ was previously reported for this region³. It is believed now that $\nu_2 + \nu_5$ was actually observed but under insufficient resolution to permit accurate identification.

The $\nu_2 + \nu_5$ band was treated in the same manner as ν_4 and a' , $\frac{1}{2}(b'+c')$ and ν_0 values were determined from the symmetric data. An attempt to use the asymmetric energy terms for sub-bands corresponding to K values less than three was unsuccessful because of the severe overlap with ν_4 .

Perhaps the most interesting feature of the $\nu_2 + \nu_5$ band is its great intensity. The fact that the fundamental band ν_4 is only four or five times as intense as the combination band suggests the possibility of a resonance interaction. Since there is no evidence of anomalous spacing of the ν_0^{sub} positions, coriolis resonance is unlikely.

The $\nu_2 + \nu_5$ band center is calculated to fall at 2993.19 cm^{-1} by using experimentally determined values of ν_2 and ν_5 and by neglecting the effects of anharmonicity. The observed value of 3003.29 cm^{-1} is significantly higher, and it is believed that the displacement is

caused by Fermi resonance with ν'_4 . The choice of ν'_4 is justified, since it is the nearest fundamental band of the same vibrational species as $\nu'_2 + \nu'_5$.

A third band which is probably ν'_1 is centered at approximately 2766.39 cm^{-1} . Positive identification is difficult, since the spectral region occupied by this band is complicated by overlapping lines of the ν'_4 band.

The ν'_1 fundamental is a type A band and because of the slight asymmetry of the formaldehyde molecule should closely resemble a parallel band of a symmetric top. The most prominent feature of such a band is the Q branch structure, which is generally unresolved and, therefore, appears as an intense, broad line. The strong line at 2766.39 cm^{-1} resembles such a Q branch. The associated P and R branch lines are hidden by a large number of strong lines that probably belong to ν'_4 and perhaps to combination and overtone bands. An attempt to identify the P and R branch lines was not successful, but in view of the complex nature of the spectrum, this failure is not considered to cast serious doubt on the identification of ν'_1 .

B. The 5.7 Micron Region

The absorption region near 5.7 microns is a region of intense absorption and is a single type A band. This band, which is centered at 1746.07 cm^{-1} , is the ν'_2 fundamental. The structure of the band is a fine example of the effects of slight asymmetry on a parallel band.

The absorption pattern of the spectral band is presented in

Figure 10. It is seen that the major features are like those of a parallel band for a symmetric top molecule. The triplet structure in the P and R branches is due to the asymmetry.

As mentioned previously, the effects of asymmetry are most pronounced for low K and high J . In addition, the ortho-para properties of the molecule introduce a 3:1 intensity alternation where sub-bands originating from odd K states contain the strong lines.

The strong central line in the triplet structure is formed from the various sub-band components for $K \geq 3$. The weaker lines on either side are the components of the $K = 1$ transition. It is clear that the splitting of these component lines increases with increasing J as predicted.

In addition to these lines, there should be a doublet series corresponding to the $K = 2$ transition and a singlet series corresponding to the $K = 0$ transition. Both of these are weak line series and, therefore, more difficult to resolve.

It has been stated that the effect of the asymmetry is greatest for low K and high J . There is one exception, and this is for $K = 0$. The single $K = 0$ level is not displaced quite as much as are the $K = 1$ levels. Consequently the $K = 0$ sub-band P and R branch lines should fall between the two components of the $K = 1$ sub-band. As is seen in Figure 10, these lines begin to split away from the strong, central component for $J = 8$ and are well resolved for $J = 10$.

P and R branch lines in the $K = 2$ sub-band were not resolved, and it is assumed that these lines contribute to the central lines in the triplets.

There are numerous weak lines on either side of the Q branch that do not fall within the $K = 1$ doublets. These lines are believed to be Q branch lines originating from the $K = 0$ or 1 transitions.

The symmetric or strong lines in the P and R branches were used to calculate values of $\frac{1}{2}(b+c)$ for the upper and lower state and a value of the band center. The relations used in these calculations are

$$R(J) - P(J) = 2(b'+c')(J + \frac{1}{2})$$

$$R(J-1) - P(J+1) = 2(b''+c'')(J + \frac{1}{2}) \quad \text{and}$$

$$R(J-1) + P(J) = 2\nu_0 + ((b'+c') - (b''+c''))J^2.$$

The calculated lower state value $\frac{1}{2}(b''+c'') = 1.2160 \text{ cm}^{-1}$ is in good agreement with the microwave value 1.21487 cm^{-1} .

A plot of $R(J) - P(J)$ vs. $(J + \frac{1}{2})$ gives a straight line whose slope is $2(b'+c')$ (Figure 11). Centrifugal distortion causes the experimental points to fall below the straight line by an amount that increases with increasing J . No such deviation was observed for values up to $J = 23$, and it is concluded that centrifugal distortion corrections are unimportant for this band. The value of $\frac{1}{2}(b'+c')$ determined from the graph is 1.2082 cm^{-1} .

The lines belonging to the $K = 1$ transition were identified by matching upper state term values. The lower state term values were calculated by using the relation

$$F'' = \frac{1}{2}(a+c)J(J+1) + \frac{1}{2}(a-c)E_r^J(\kappa).$$

The upper state term was then obtained from $F' = F'' + \nu$. Since one line in the P branch and one line in the R branch have the same upper state, an unambiguous assignment was possible.

An attempt was made to determine $\mathcal{K}'$, a' , b' , and c' by using the asymmetric formulation. If two upper state terms with the same J value but different τ values are subtracted, there results $F'(J_{\tau_1}) - F'(J_{\tau_2}) = \frac{1}{2} (a' - c') (E_{\tau_1}^J - E_{\tau_2}^J)$. A plot of $a' - c'$ versus $\mathcal{K}'$ then gives a curve representing compatible values of the two quantities. If a number of such curves are plotted, they should intersect at a point. This permits graphical evaluation of $\mathcal{K}'$ and $(a' - c')$. These values are then substituted in the term expressions to obtain a value for $(a' + c')$. Finally, the defining relation $\mathcal{K} = \frac{2b - (a + c)}{a - c}$ is used to obtain a value for b' .

This method is most sensitive when the numerical values of the terms differ by a large amount and when pairs of terms corresponding to large K differences are used. In the present case, the plots obtained were closely spaced, nearly parallel lines. The failure of the plots to give a value of $\mathcal{K}$ is not surprising, since the terms differed by but a few wavenumbers and all corresponded to the same value of K .

The values of the rotational constants determined from the symmetric data are listed in Table 1. The errors listed for the rotational constants are the square roots of the sum of the squares of the deviations of the experimental points from the most probable straight line through the points as determined by the method of least squares.

C. The 6.7 Micron Region

The formaldehyde band at 6.7 microns is a second type A band designated as ν_3 . This spectral region is one of intense absorption for water vapor and lack of a suitable vacuum instrument prevented previous

investigators from resolving the band. Using the vacuum instrument described above, it was possible to eliminate all but a few very strong water vapor lines. These lines are located at the extreme edge of the R branch of the formaldehyde band, and so do not obscure the absorption pattern.

A photograph of the ν_3 band is presented in Figure 11. It is immediately apparent that the structure of this band differs considerably from that of ν_2 . The Q branch is partially resolved and is shaded toward higher frequencies. This reversal of the Q branch shading means that $\frac{1}{2}(b'+c') > \frac{1}{2}(b''+c'')$ and consequently the R branch diverges while the P branch converges.

The characteristic triplet structure in the P and R branches is not present. Instead there is a large number of lines which may be grouped into six or seven series. The number of these lines is seen to increase with increasing J.

The strong series of lines that correspond to effective symmetric top transitions is present in this band. The series stands out sharply in the P branch and can be located in the R branch with little difficulty.

The ν_3 band is coupled by rotational resonance to the ν_5 band. It is believed that this resonance interaction is responsible for the observed deviations from the simple type A structure. Although this particular sort of rotational resonance has not been treated theoretically, its effects can be discussed in a qualitative manner.

Transitions where $J = K$ correspond to the classical case of simple

rotation about the top axis. In this case, there is classically no coupling between the two vibrations. As a consequence of these considerations, it is expected that transitions for which $J = K$ will be but slightly influenced by the interaction. The lines resulting from these transitions probably contribute to the strong, apparently symmetric P and R branch series.

These lines alone are not sufficient to account for the strength of the series. Upper state terms were calculated assuming that transitions for $K \geq 3$ also contribute to the series. The calculated term values indicate that the assumption is justified for the limited range of J values for which lower state terms could be calculated. Since the number of P and R branch lines increases with increasing J, it appears that this relation is not valid for values of J greater than approximately 12.

The two series corresponding to the $K = 1$ transition were identified by using the method described for ν_2 . One of these series coincides with the strong series in the R branch and the other coincides with the strong series in the P branch. Since the asymmetric rotator tables do not extend beyond $J = 12$, only a few term values could be calculated. The coincidence in the P branch is nearly perfect while that in the R branch breaks down for $J = 7$ and the $K = 1$ lines split away from the strong component for values of J larger than 7.

The remaining lines of the $K = 1$ transition were identified as the series of lines lying on the low frequency side of the strong series in both the P and R branches. These lines are easily recognized since

for low J they form the second strongest series of lines in the spectrum.

The effect of the interaction on lines corresponding to the $K = 1$ transition is a shift in the direction of decreasing frequency.

It is interesting to note that lines in the P branch are more intense than those in the R branch. This is particularly evident for high J. This situation is probably analogous to that described by the Teller-Tiza intensity selection rule mentioned earlier.

Attempts to identify other weak line series were not successful.

Upper and lower state $\frac{1}{2}(b+c)$ values and a value of ν_0 were obtained by using the strong line series. These values $\frac{1}{2}(b'+c') = 1.221 \text{ cm}^{-1}$, $\frac{1}{2}(b''+c'') = 1.217 \text{ cm}^{-1}$ were calculated by using the symmetric top combination - difference relations described for ν_2 . The effects of centrifugal distortion were not apparent for $J \leq 15$. The ground state value determined for $\frac{1}{2}(b''+c'')$ differs by 0.002 cm^{-1} from the microwave value. This difference is probably due to the fact that the strong series of lines is effected slightly by the rotational resonance interaction. The errors reported here are root means square deviations.

D. The 7.5 to 10 Micron Region

The spectral region extending from 7.5 to 10 microns contains the two fundamental bands ν_5 and ν_6 . The bands are type B and type C respectively and have very similar forms in those regions where the effects of the asymmetry are small. The differences in the rotational

selection rules for the two types of bands introduce important variations in the rotational structure corresponding to low K transitions. These variations permit an unambiguous assignment of the two fundamentals.

The two bands (Figures 12 to 16) are closely spaced and overlap badly in the central portion of the spectrum. In spite of the overlapping, a number of strong lines stand out rather sharply. These are the Q branches corresponding to $\Delta K = -1$ and $\Delta K = +1$ transitions for ν_5 and ν_6 respectively. The associated P and R branches are rather difficult to find.

The structure in the extremities of the band is easier to interpret. The Q branches which correspond to $\Delta K = +1$ and $\Delta K = -1$ for ν_5 and ν_6 respectively as well as their associated P and R branches are readily identified. Assignment of lower state K value for the various sub-bands is facilitated by the observation of missing lines near the sub-band centers in the P and R branches.

It is seen that the sub-bands originating from odd K ground states are more intense than those originating from even K states. The intensity alternation is in the ratio of 3:1 as predicted from theoretical considerations.

The ν_5 and ν_6 bands are separated by approximately 80 cm^{-1} and interact strongly. The effects of the rotational resonance are quite pronounced.

The Q branches in the extremities of the band are spaced far apart. The largest observed spacing is approximately 25 cm^{-1} . The spacing

decreases slowly as the two band centers are approached.

The Q branches in the adjacent or overlapping portions of the bands are considerably closer together than those in the extremities. The spacing increases as the band centers are approached.

The rotational structure in regions of the bands where the effects of asymmetry are large is more difficult to interpret. The Q branches are at least partially resolved and lines in the P and R branches no longer exhibit regular spacing. Careful treatment shows, however, that the above mentioned considerations apply to these regions without modification.

According to the selection rule of Teller and Tiza, the rotational lines corresponding to $\Delta K = -1$ and $\Delta K = +1$ for ν_5 and ν_6 respectively should be more intense than those corresponding to $\Delta K = +1$ and $\Delta K = -1$, respectively. No such effect is apparent, and it appears that the intensity selection rule is not important in this case.

A partial analysis can be effected by using lines from the symmetric portions of the two bands. The upper state energy term is

$$F(J) = \nu_5 + \nu_6 + \frac{1}{2}(b'+c')J'(J'+1) + a'J^2 + (a' - \frac{1}{2}(b'+c')) \\ (K'^2+1) \pm \left(\frac{(\nu_5 - \nu_6)^2}{4} + 4a'^2 J^2 K'^2 \right) ,$$

where it is assumed that the effects of asymmetry are negligible. Since the plus sign is taken with ν_5 and the minus sign with ν_6 , subtraction of two terms with the same J and K value gives

$$\Delta F = 2 \left(\frac{(\nu_5 - \nu_6)^2}{4} + 4a'^2 J^2 K'^2 \right) .$$

Two such equations written for different values of K' can be solved simultaneously and $\nu_5 - \nu_6$ and $a'^2 f^2$ can be evaluated.

The constants $a'^2 f^2 = 25.88 \pm 0.04 \text{ cm}^{-2}$ and $\nu_5 - \nu_6 = 83.95 \pm 0.15 \text{ cm}^{-1}$ were obtained in this manner. A large number of equations for $K' = 4$ and $K' = 6$ was used. The $K' = 4$ equations were formed from upper state terms obtained from the $\nu_5 K'' = 3$, $\Delta K = +1$, $\Delta J = +1$ series and the $\nu_6 K'' = 5$, $\Delta K = -1$, $\Delta J = -1$ series. The $K' = 6$ equations were formed from the upper state terms for the $\nu_5 K'' = 5$, $\Delta K = +1$, $\Delta J = +1$ and the $\nu_6 K'' = 7$, $\Delta K = -1$, $\Delta J = -1$ series. The errors reported above are averages of the absolute values of the deviations of the constants from the values determined by using the several sets of simultaneous equations.

Addition of two upper state terms with the same J and K gives

$$\sum F = 2(\nu_5 + \nu_6) + 2a'f^2 + 2K'^2(a' - \frac{1}{2}(b'+c')) + (b'+c')J'(J'+1).$$

A plot of $\sum F$ as a function of $J'(J'+1)$ gives a straight line with slope $(b'+c')$ and intercept $2(\nu_5 + \nu_6) + 2a'f^2 + 2K'^2(a' - \frac{1}{2}(b'+c'))$.

The value $\frac{1}{2}(b'+c') = 1.212 \pm 0.002 \text{ cm}^{-1}$ was determined in this manner from two sets of data, one corresponding to $K' = 4$ and the other to $K' = 6$. The slopes and intercepts were calculated by using the method of least squares. The errors are root mean square deviations of the experimental points from the points representing the most probable straight line.

The difference between the two intercepts is $40(a' - \frac{1}{2}(b'+c'))$. This relation was used with the value of $(b'+c')$ to evaluate $a' =$

$$9.394 \pm 0.003 \text{ cm}^{-1}.$$

Finally the $\sum F$ equations were solved for $\nu_5 + \nu_6$ using the previously determined constants. Sufficient information was then available to determine unique values for ν_5 and ν_6 . The calculated values of the band centers, rotational constants and Coriolis coupling constants are listed in Table 1.

In order to determine independent values of b' and c' , it is necessary to use data from the portions of the spectrum where the effective asymmetry is large. Identification of the asymmetric rotational lines is difficult, since there is no obvious regularity.

The energy term for the asymmetric lines is

$$F = (\nu_5 + \nu_6) + \frac{1}{2}(a' + c')J'(J'+1) + \frac{1}{2}(a' - c')E_{\tau'}^{J'}(\kappa') + a'\gamma^2 \\ \pm \left[\left(\frac{\nu_5 - \nu_6}{2} \right)^2 + 4a'\gamma^2 \left(\frac{(a' - c')E_{\tau'}^{J'}(\kappa') + (a' - b')J'(J'+1)}{2(a' - \frac{1}{2}(b' + c'))} \right) \right]^{1/2}$$

The sum of a term from ν_5 and a term from ν_6 having the same J' and τ' is

$$\sum F = 2(\nu_5 + \nu_6) + 2a'\gamma^2 + (a' + c')J'(J'+1) + (a' - c')E_{\tau'}^{J'}(\kappa')$$

If the values of the constants determined from the symmetric region analysis are used, c' can be expressed as a function of $E_{\tau'}^{J'}(\kappa')$.

This function can be expressed graphically if values of $E_{\tau'}^{J'}(\kappa')$ are calculated from the asymmetric rotator tables. A number of plots for different J' and τ' intersect at a point which permits graphical determination of c' and κ' . This method is sensitive when a number of curves corresponding to widely different K' values are used.

The sub-band corresponding to $K'' = 1, \Delta K = -1$ has a singlet structure since there is but one $K' = 0$ level for each value of J' . Consequently, it is not difficult to identify the lines in these sub-bands by matching upper state energy terms. The two sub-bands are easily recognized by their relatively open structure and are located at approximately 1240 cm^{-1} and 1160 cm^{-1} .

The Q branch for the ν'_5 sub-band at 1240 cm^{-1} is shaded toward lower frequencies. The selection rules for a type C band require the Q branch in the ν'_6 band corresponding to the same transitions to be shaded toward higher frequencies. This effect is observed in the Q branch at 1160 cm^{-1} and justifies the assignment of ν'_6 as the low frequency fundamental.

Lines in the P, Q, and R branches of each of these sub-bands were identified and average upper state term values were calculated for values of J ranging from 4 to 12. These terms were then used in the relation expressing c' as a function of κ' to determine a value for c' and κ' . In addition, suitable upper state terms calculated from the symmetric region data were used.

Figure 18 shows a number of plots of c' vs. κ' for several pairs of upper state energy terms. The straight line marked S is representative of the symmetric region energy terms and also c' vs. κ' as determined from the equation $\kappa' = \frac{2b-a-c}{a-c}$ which defined κ' . This line has a larger weight than the individual lines that represent the asymmetric energy terms.

The values $\kappa' = -0.962 \pm 0.001$ and $c' = 1.133 \pm 0.002 \text{ cm}^{-1}$ were

determined from the best point of intersection. The errors were estimated. The constants determined from the analysis of the ν'_5 and ν'_6 bands are listed in Table 1.

Ebers and Nielsen⁴ carried out a partial analysis of the ν'_5 and ν'_6 bands. The constants $\nu'_5 = 1278 \text{ cm}^{-1}$, $\nu'_6 = 1165 \text{ cm}^{-1}$ and $J = 0.6$ were determined from a spectral trace in which only the Q branches were well resolved. In view of the difference in resolution between the spectra recorded by Ebers and Nielsen and those recorded for this study, the agreement among the constants is satisfactory.

SUMMARY

In conclusion, the results of this investigation will be briefly summarized.

The infrared absorption spectrum of formaldehyde vapor in the region extending from 3 to 10 microns has been recorded under high resolution. All six of the fundamental bands were observed and band-center frequencies reported. In addition, a weak band at 3003.29 cm^{-1} , that was previously reported as $2\nu'_3$, has been identified as $\nu'_2 + \nu'_5$. It appears that this band is coupled to ν'_4 by a vibrational resonance.

The bands designated as ν'_4 , ν'_3 , and $\nu'_2 + \nu'_5$ were partially analysed, and ν'_2 was completely analysed. The two bands ν'_5 and ν'_6 , which are strongly coupled by a rotational resonance interaction, were treated by using the theory of Nielsen. Complete analysis of these bands was possible and values for the rotational constants and the Coriolis coupling constant were obtained. In addition, the assignment of the low frequency band as ν'_6 was verified.

CELL I

FIGURE I

CELL 2

FIGURE 2

PRISM GRATING HIGH
DISPERSION INFRA-RED
SPECTROMETER

FIGURE 3

FIGURE 4

ν_1 ν_2 ν_3 ν_4 ν_5 ν_6

NORMAL MODES OF VIBRATION

FIGURE 5

H_2CO 5.7 MICRON REGION

FIGURE 10

FIGURE 11

H_2CO 6.7 MICRON REGION

FIGURE 12

FIGURE 13

FIGURE 14

FIGURE 15

FIGURE 16

FIGURE 17

FIGURE 18

PRISM TRACE H_2CO VAPOR
ABSORPTION SPECTRUM

FIGURE 19

TABLE 1

The Constants

A. The ν_4 Band

$$\nu_0 = 2843.4 \pm 0.2 \text{ cm}^{-1}$$

$$a' = 9.200 \pm 0.004 \text{ cm}^{-1}$$

$$\frac{1}{2}(b'+c') = 1.207 \pm 0.001 \text{ cm}^{-1}$$

B. The $\nu_2 + \nu_5$ Band

$$\nu_0 = 3003.3 \pm 0.1 \text{ cm}^{-1}$$

$$a' = 10.061 \pm 0.002 \text{ cm}^{-1}$$

$$\frac{1}{2}(b'+c') = 1.203 \pm 0.001 \text{ cm}^{-1}$$

C. The ν_1 Band

$$\nu_0 = 2766.4 \pm 0.4 \text{ cm}^{-1}$$

D. The ν_2 Band

$$\nu_0 = 1746.07 \pm 0.05 \text{ cm}^{-1}$$

$$\frac{1}{2}(b'+c') = 1.208 \pm 0.001 \text{ cm}^{-1}$$

$$\frac{1}{2}(b''+c'') = 1.216 \pm 0.001 \text{ cm}^{-1}$$

E. The ν_3 Band

$$\nu_0 = 1500.58 \pm 0.08 \text{ cm}^{-1}$$

$$\frac{1}{2}(b'+c') = 1.221 \pm 0.001 \text{ cm}^{-1}$$

$$\frac{1}{2}(b''+c'') = 1.217 \pm 0.001 \text{ cm}^{-1}$$

TABLE 1

Continued

F. The ν'_5 and ν'_6 Bands

$$(\nu'_5) \nu'_0 = 1247.44 \pm 0.08 \text{ cm}^{-1}$$

$$(\nu'_6) \nu'_0 = 1163.49 \pm 0.08 \text{ cm}^{-1}$$

$$S = 0.541 \pm 0.001$$

$$K' = -0.962 \pm 0.001$$

$$\frac{1}{2}(b'+c') = 1.2116 \pm 0.002 \text{ cm}^{-1}$$

$$a' = 9.394 \pm 0.003 \text{ cm}^{-1}$$

$$b' = 1.290 \pm 0.002 \text{ cm}^{-1}$$

$$c' = 1.133 \pm 0.002 \text{ cm}^{-1}$$

G. Microwave Values⁷

$$a'' = 9.41056 \text{ cm}^{-1}$$

$$b'' = 1.29543 \text{ cm}^{-1}$$

$$c'' = 1.13431 \text{ cm}^{-1}$$

$$K'' = -0.961$$

TABLE 2
The 3 to 4 Micron Region Line Frequencies*

Line Number	Identification	Frequency Cm^{-1}
1		3199.60
2		3197.76
3		3195.97
4		3193.96
5		3191.92
6		3189.91
7		3187.91
8		3185.76
9		3185.27
10		3184.52
11		3183.70
12		3178.10
13		3169.63
14		3167.94
15		3165.97
16		3163.88
17		3163.61
18		3162.09
19		3159.61
20	$\text{R}_{\text{R}'_5}(18)$	3158.44
21		3157.39
22	$\text{R}_{\text{R}'_5}(17)$	3156.57
23	$\text{R}_{\text{R}'_5}(16)$	3154.58
24	$\text{R}_{\text{R}'_5}(15)$	3152.63
25	$\text{R}_{\text{R}'_5}(14)$	3150.56
26	$\text{R}_{\text{R}'_5}(13)$	3148.53
27	$\text{R}_{\text{R}'_5}(12)$	3146.47
28	$\text{R}_{\text{R}'_5}(11)$	3144.44
29	$\text{R}_{\text{R}'_5}(10)$	3142.34
30	$\text{R}_{\text{R}'_5}(9)$	3140.20
31	$\text{R}_{\text{R}'_5}(8)$	3137.99

* R'_5 refers to the $\nu_2 + \nu_5$ band while R_5 refers to the ν_4 band.

TABLE 2
Continued

Line Number	Identification	Frequency Cm^{-1}
32	$R_{R_5}(7)$	3135.81
33	$R_{R_4}(18)$	3135.11
34		3134.46
35	$R_{R_5}(6), R_{R_4}(17)$	3133.55
36		3132.97
37	$R_{R_5}(5), R_{R_4}(16)$	3131.29
38	$R_{R_4}(15)$	3129.32
39	$R_{R_4}(14)$	3127.34
40		3126.65
41	$R_{R_4}(13)$	3125.15
42	$R_{R_4}(12)$	3123.13
43		3122.27
44	$R_{R_4}(11)$	3121.08
45		3119.62
46	$R_{R_4}(10)$	3118.87
47		3117.96
48		3117.49
49	$R_{R_4}(9)$	3116.74
50		3116.22
51		3115.86
52		3115.25
53		3115.01
54	$R_{R_4}(8)$	3114.70
55		3114.26
56		3113.69
57		3113.33
58	$R_{R_4}(7)$	3112.37
59		3111.87
60	$R_{R_3}(17)$	3110.91
61	$R_{R_4}(6)$	3110.20
62		3109.48
63	$R_{R_3}(16)$	3109.02
64	$R_{R_4}(5)$	3108.14

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
65		3107.13
66	$R_{R_3}^1(15)$	3106.69
67		3106.36
68	$R_{R_4}^1(4)$	3105.65
69	$R_{R_3}^1(14)$	3104.47
70		3103.71
71	$R_{R_3}^1(13)$	3102.67
72		3101.20
73	$R_{R_3}^1(12)$	3100.52
74		3100.27
75		3009.51
76	$R_{R_3}^1(11)$	3098.45
77		3096.87
78	$R_{R_3}^1(10)$	3096.30
79		3095.92
80		3095.17
81		3094.63
82	$R_{R_3}^1(9)$	3094.12
83		3093.17
84		3092.73
85	$R_{R_3}^1(8)$	3091.92
86		3091.21
87		3090.81
88	$R_{R_3}^1(7)$	3089.70
89		3088.92
90		3088.35
91	$R_{R_3}^1(6)$	3087.46
92		3086.88
93		3085.90
94	$R_{R_3}^1(5)$	3085.20
95		3084.66
96		3083.80
97	$R_{R_3}^1(4)$	3083.51
98		3081.41
99	$R_{R_3}^1(3)$	3080.65
100		3079.55
101		3078.83
102		3077.95
103		3077.22

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
104		3076.53
105		3075.88
106		3075.32
107		3074.95
108		3074.36
109		3073.64
110		3072.60
111		3072.36
112		3071.77
113		3070.39
114		3070.25
115		3070.07
116		3069.78
117		3069.48
118		3069.22
119		3068.79
120		3068.34
121		3067.81
122		3067.51
123		3067.06
124		3066.19
125		3065.74
126		3065.47
127		3065.02
128		3064.28
129		3063.64
130		3063.30
131		3062.98
132		3062.63
133		3062.42
134		3062.00
135		3061.55
136		3061.07
137		3060.81
138		3059.88
139		3059.12
140		3058.67
141		3057.72
142		3057.09
143		3056.33
144		3055.88
145		3055.54
146		3055.09
147		3054.59

TABLE 2

Continued

Line Number	Identification	Frequency cm^{-1}
148		3054.36
149		3054.07
150		3053.57
151		3053.41
152		3053.22
153		3052.70
154		3052.20
155		3051.62
156		3051.41
157		3051.04
158		3050.94
159		3050.83
160		3050.20
161		3049.58
162		3048.84
163		3048.61
164		3048.45
165		3048.03
166		3047.53
167		3046.67
168		3046.07
169		3045.60
170		3044.84
171		3044.21
172		3043.69
173		3043.30
174		3042.20
175		3041.55
176		3041.26
177		3040.56
178		3040.07
179		3039.73
180		3039.34
181		3038.64
182		3048.40
183		3037.70
184		3037.28
185		3036.66
186		3036.22
187		3035.70
188		3035.05
189		3034.15
190		3033.68

TABLE 2

Continued

Line Number	Identification	Frequency Cm ⁻¹
191		3033.01
192		3032.51
193		3032.23
194		3031.66
195		3031.17
196		3030.42
197		3029.98
198		3029.57
199		3028.53
200		3028.84
201		3028.31
202		3027.74
203		3027.55
204		3026.81
205		3026.34
206		3025.78
207		3025.49
208		3025.37
209		3025.13
210		3024.90
211		3024.65
212		3024.29
213		3024.03
214		3023.41
215		3023.05
216		3022.72
217		3022.59
218		3022.26
219		3021.43
220		3020.79
221		3020.28
222		3019.92
223		3019.23
224		3018.34
225		3017.93
226		3017.60
227		3017.19
228		3016.55
229		3016.32
230		3015.66
231		3015.56
232		3014.92
233		3014.56

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
234		3013.62
235		3013.98
236		3012.32
237		3011.63
238		3011.14
239		3010.69
240		3009.97
241		3009.62
242		3009.03
243		3008.45
244		3007.69
245		3007.46
246		3007.03
247		3006.32
248		3005.83
249		3005.40
250		3005.25
251		3004.54
252		3004.49
253		3003.96
254		3003.05
255		3002.67
256		3002.37
257		3001.81
258		3001.27
259		3000.75
260		2999.12
261		2999.71
262		2999.18
263		2998.98
264		2998.45
265		2997.80
266		2997.57
267		2997.12
268		2996.89
269		2996.54
270		2996.16
271		2995.81
272		2995.46
273		2995.00
274		2994.63
275		2994.23
276		2993.72

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
277		2993.30
278		2992.79
279		2992.19
280		2991.51
281		2990.74
282		2900.26
283		2989.59
284		2989.11
285		2988.94
286		2988.59
287		2987.93
288		2987.34
289		2986.86
290		2986.29
291		2985.89
292		2985.56
293		2984.96
294		2984.49
295		2924.13
296		3983.72
297		2983.27
298		2982.75
299		2982.45
300		2982.22
301		2981.87
302		2981.57
303		2981.40
304		2980.73
305		2980.46
306		2979.99
307	$\text{R}_{\text{R}6}(16)$	2979.57
308		2979.35
309		2978.68
310		2978.21
311	$\text{R}_{\text{R}6}(15)$	2977.71
312		2977.51
313		2976.52
314		2976.00
315		2975.73
316	$\text{R}_{\text{R}6}(14)$	3974.99
317		2974.49
318		2974.07

TABLE 2

Continued

Line Number	Identification	Frequency cm^{-1}
319		2973.90
320		2973.80
321		2973.38
322	$R_{R_6}(13)$	2972.78
323	$R_{R_5}(19)$	2972.32
324		2971.82
325		2971.55
326		2971.20
327	$R_{R_6}(12)$	2970.61
328	$R_{R_5}(18)$	2970.19
329		2969.65
330		2969.33
331		2969.18
332		2968.86
333		2968.59
334		2968.49
335	$R_{R_6}(11)$	2968.39
336	$R_{R_5}(17)$	2968.00
337		2967.41
338		2967.07
339		2966.72
340		2966.35
341	$R_{R_6}(10)$	2966.11
342	$R_{R_5}(16)$	2965.84
343		2965.22
344		2964.78
345		2964.61
346		2964.36
347	$R_{R_6}(9)$	2963.85
348	$R_{R_5}(15)$	2963.75
349		2963.60
350		2963.36
351		2963.21
352		2962.75
353		2962.65
354		2962.11
355	$R_{R_6}(18), R_{R_5}(14)$	2961.45
356		2960.91
357		2960.54

TABLE 2
Continued

Line Number	Identification	Frequency Cm^{-1}
358		2960.05
359		2959.88
360		2959.73
361		2959.68
362		2959.54
363	$\text{R}_{\text{R}_6}(7), \text{R}_{\text{R}_5}(13)$	2959.12
364		2958.95
365		2958.51
366		2958.37
367		2958.22
368		2958.10
369		2957.61
370		2957.22
371	$\text{R}_{\text{R}_6}(6), \text{R}_{\text{R}_5}(12)$	2956.88
372		2956.24
373		2956.10
374		2955.63
375		2955.17
376	$\text{R}_{\text{R}_5}(11)$	2954.58
377		2954.10
378		2953.64
379		2953.22
380		2953.00
381		2952.59
382	$\text{R}_{\text{R}_5}(10)$	2952.30
383		2951.76
384		2951.50
385		2951.33
386		2951.13
387		2950.86
388		2950.55
389		2950.33
390	$\text{R}_{\text{R}_5}(9)$	2949.99
391	$\text{R}_{\text{R}_4}(15)$	2949.63
392		2949.34
393		2948.92
394		2948.24
395		2947.98
396	$\text{R}_{\text{R}_5}(8)$	2947.66
397	$\text{R}_{\text{R}_4}(14)$	2947.35
398		2946.49

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
399		2946.49
400	$\text{R}_{\text{R}_5}(7)$	2945.34
401	$\text{R}_{\text{R}_4}(13)$	2945.05
402		2944.76
403		2944.49
404		2943.48
405	$\text{P}_{\text{R}_5}(6), \text{P}_{\text{R}_4}(12)$	2942.90
406		2943.61
407		2942.18
408		2941.46
409	$\text{P}_{\text{R}_3}(18)$	2940.98
410	$\text{P}_{\text{R}_5}(5), \text{P}_{\text{R}_4}(11)$	2940.57
411		2939.78
412		2939.61
413	$\text{P}_{\text{R}_3}(17)$	2939.01
414		2938.77
415	$\text{P}_{\text{R}_4}(10)$	2938.14
416		2937.57
417	$\text{P}_{\text{R}_3}(16)$	2936.97
418		2936.85
419	$\text{P}_{\text{R}_4}(9)$	2935.93
420		2935.24
421	$\text{P}_{\text{R}_3}(15)$	2934.79
422		2934.57
423	$\text{P}_{\text{R}_4}(8)$	2933.56
424		2932.84
425	$\text{P}_{\text{R}_3}(14)$	2932.65
426		2931.86
427	$\text{P}_{\text{R}_4}(7)$	2931.26
428	$\text{P}_{\text{R}_3}(13)$	2930.55
429		2929.93
430		2929.23
431	$\text{P}_{\text{R}_4}(6)$	2928.88
432	$\text{P}_{\text{R}_3}(12)$	2928.26
433		2927.37
434		2926.90
435		2926.52

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
436	$\text{P}_{\text{R}_4}(5)$	2925.95
437		2925.59
438		2925.33
439		2925.06
440		2924.85
441		2924.61
442		2924.40
443		2924.23
444	$\text{R}_{\text{R}_4}(4)$	2923.69
445	$\text{R}_{\text{R}_3}(10)$	2922.97
446		2922.67
447		2922.36
448		2921.95
449		2921.38
450	$\text{R}_{\text{R}_3}(9)$	2921.15
451		2920.34
452		2920.10
453		2919.82
454	$\text{R}_{\text{R}_3}(8)$	2919.01
455		2918.23
456		2917.83
457		2917.05
458		2916.77
459	$\text{R}_{\text{R}_3}(7)$	2916.34
460		2915.40
461		2914.95
462		2914.38
463	$\text{R}_{\text{R}_3}(16)$	2913.94
464		2913.35
465		2912.38
466		2911.82
467		2911.58
468		2911.23
469		2910.76
470		2910.22
471		2909.65
472	$\text{R}_{\text{R}_3}(4)$	2909.23
473		2908.53
474		2908.03
475		2907.78
476	$\text{R}_{\text{R}_3}(3)$	2907.28

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
477		2906.77
478		2906.32
479		2905.64
480		2905.20
481		2904.99
482		2904.64
483		2904.33
484		2903.47
485		2903.21
486		2902.63
487		2902.23
488		2901.95
489		2901.18
490		2900.76
491		2900.20
492		2899.53
493		2899.14
494		2898.81
495		2898.53
496		2898.04
497		2896.95
498		2896.81
499		2896.16
500		2895.84
501		2895.59
502		2895.59
503		2894.56
504		2893.91
505		2893.70
506		2893.24
507		2892.82
508		2892.43
509		2892.29
510		2891.85
511		2891.52
512		2891.32
513		2890.89
514		2890.44
515		2889.79
516		2888.96
517		2888.62
518		2888.22
519		2887.83
520		2887.34

TABLE 2.

Continued

Line Number	Identification	Frequency cm ⁻¹
521		2886.97
522		2886.56
523		2886.21
524		2885.70
525		2885.27
526		2885.71
527		2884.17
528		2883.47
529		2883.38
530		2882.83
531		2882.35
532		2881.79
533		2881.42
534		2880.99
535		2880.40
536		2879.98
537		2879.39
538		2878.93
539		2878.56
540		2878.31
541		2878.15
542		2977.92
543		2877.37
544		2876.32
545		2876.18
546		2875.63
547		2875.31
548		2874.95
549		2874.58
550		2874.33
551		2873.58
552		2872.85
553		2872.26
554		2871.89
555		2871.14
556		2870.39
557		2879.69
558		2869.46
559		2869.12
560		2868.62
561		2868.12
562		2867.66
563		2867.03
564		2866.46

TABLE 2

Continued

Line Number	Identification	Frequency Cm ⁻¹
565		2866.21
566		2865.76
567		2865.28
568		2864.85
569		2864.31
570		2863.93
571		2863.45
572		2863.09
573		2862.70
574		2862.18
575		2862.00
576		2861.53
577		2861.13
578		2860.59
579		2860.01
580		2859.51
581		2858.65
582		2858.91
583		2857.30
584		2856.85
585		2856.00
586		2855.10
587		2854.00
588		2854.22
589		2854.82
590		2853.37
591		2853.24
592		2852.88
593		2852.34
594		2851.94
593		2851.65
596		2851.29
597		2850.93
598		2850.62
599		2850.48
600		2849.85
601		2849.48
602		2849.18
603		2848.96
604		2848.78
605		2848.63
606		2848.45
607		2847.69
608		2847.35

TABLE 2

Continued

Line Number	Identification	Frequency cm^{-1}
609		2846.88
610		2846.71
611		2846.28
612		2846.06
613		2845.75
614		2845.12
613		2844.66
616		2844.28
617		2843.68
618		2843.30
619		2843.08
620		2842.48
621		2842.08
622		2841.45
623		2841.28
624		2841.03
625		2840.61
626		2839.95
627		2839.57
628		2838.90
629		2828.79
630		2838.26
631		2837.93
632		2837.55
633		2837.09
634		2836.89
635		2836.56
636		2836.25
637		2835.98
638		2835.63
639		2835.14
640		2834.75
641		2834.59
642		2834.22
643		2833.71
644		2833.14
645		2832.74
646		2832.23
647		2832.17
648		2831.61
649		2831.31
650		2830.54
651		2829.59
652		2829.33

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
653		2829.04
654		2828.47
655		2828.21
656		2827.54
657		2827.06
658		2826.93
659		2826.69
660		2826.17
661		2825.99
662		2825.36
663		2825.05
664		2824.65
665		2824.30
666		2824.10
667		2823.65
668		2823.30
669		2822.78
670		2822.00
671		2821.25
672		2820.90
673		2820.42
674		2820.16
675		2819.97
676		2819.60
677		2819.03
678		2818.44
679		2818.25
680		2817.68
681		2817.20
682		2816.74
683		2816.29
684		2816.16
685		2815.27
686		2814.70
687		2814.44
688		2814.27
689		2813.60
690		2812.90
691		2812.29
692		2811.43
693		2811.00
694		2810.63
695		2810.35

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
696		2809.81
697		2809.37
698		2809.03
699		2808.79
700		2808.60
701		2808.34
702		2807.92
703		2807.41
704		2807.21
705		2806.88
706		2806.44
707		2806.16
708		2805.90
709		2805.45
710		2805.02
711		2804.94
712		2804.16
713		2803.92
714		2803.68
715		2803.15
716		2802.67
717		2802.35
718		2801.53
719		2800.85
720		2800.29
721		2799.90
722		2799.39
723		2799.22
724		2798.91
725		2798.61
726		2798.13
727		2797.81
728		2797.66
729		2797.31
730		2796.90
731		2796.24
732		2795.05
733		2795.45
734		2794.91
735		2794.32
736		2993.94
737		2793.70
738		2793.04
739		2792.70

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
740		2792.28
741		2791.87
742		2791.53
743		2791.04
744		2790.65
745		2789.70
746		2789.38
747		2789.24
748		2789.04
749		2788.45
750		2788.05
751		2787.71
752		2787.24
753		2786.94
754		2786.12
755		2785.88
756		2785.61
757		2785.31
758		2785.04
759		2784.57
760		2784.31
761		2783.76
762		2783.33
763		2783.04
764		2782.70
765		2782.26
766		2781.94
767		2781.79
768		2781.24
769		2790.84
770		2790.40
771		2779.71
772		2779.43
773		2778.78
774		2778.36
775		2777.83
776		2777.60
777		2777.18
778		2776.68
779		2776.17
780		2775.79
781		2775.42
782		2775.16

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
783		2774.45
784		2774.28
785		2773.40
786		2773.01
787		2772.73
788		2772.42
789		2772.19
790		2771.27
791		2771.04
792		2770.85
793		2770.43
794		2770.29
795		2769.70
796		2769.33
797		2768.74
798		2768.14
799		2767.84
800		2767.24
801		2766.68
802		2766.39
803		2765.87
804		2765.53
805		2765.35
806		2764.80
807		2763.91
808		2764.41
809		2763.08
810		2762.87
811		2762.27
812		2761.79
813		2761.44
814		2761.09
815		2760.78
816		2760.38
817		2760.03
818		2759.74
819		2759.37
820		2758.96
821		2758.81
822		2758.42
823		2757.92
824		2757.69
825		2757.30

TABLE 2

Continued

Line Number	Identification	Frequency cm^{-1}
826		2756.48
827		2756.15
828		2755.34
829		2754.90
830		2754.04
831		2753.92
832		2753.42
833		2753.07
834		2752.79
835		2752.38
836		2751.61
837		2750.98
838		2750.59
839		2749.93
840		2749.44
841		2749.11
842		2748.62
843		2748.21
844		2747.63
845		2748.47
846		2747.12
847		2746.63
848		2746.30
849		2745.99
850		2745.70
851		2745.47
852		2745.11
853		2744.92
854		2744.60
855		2744.11
856		2743.72
857		2743.21
858		2742.47
859		2742.05
860		2741.47
861		2741.05
862		2740.70
863		2740.29
864		2739.93
865		2739.52
866		2739.15
867		2739.09
868		2738.48

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
869		2738.24
870		2737.94
871		2737.69
872		2737.49
873		2737.23
874		2737.02
875		2736.68
876		2736.47
877		2736.01
878		2735.83
879		2735.54
880		2734.87
881		2734.47
882		2734.10
883		2733.84
884		2733.42
885		2733.13
886		2732.85
887		2732.30
888		2731.92
889		2731.65
890		2731.21
891		2730.65
892		2730.25
893		2730.02
894		2729.48
895		2729.40
896		2729.18
897		2728.89
898		2728.33
899		2728.19
900		2728.03
901		2727.42
902		2727.03
903		2726.74
904		2726.50
905		2726.10
906		2725.80
907		2725.31
908		2725.13
909		2724.91
910		2724.47
911		2724.27

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
912		2723.95
913		2723.71
914		2723.47
915		2723.17
916		2722.81
917		2722.43
918		2722.03
919		2721.75
920		2721.33
921		2721.05
922		2720.45
923		2720.37
924		2719.91
925		2719.49
926		2719.31
927		2718.91
928		2718.73
929		2718.45
930		2718.25
931		2717.49
932		2716.99
933		2716.75
934		2716.39
935		2716.12
936		2715.80
937		2715.68
938		2715.46
939		2714.92
940		2714.56
941		2714.36
942		2713.97
943		2713.81
944		2713.57
945		2718.11
946		2712.52
947		2712.34
948		2712.00
949		2711.92
950		2711.60
951		2711.29
952		2710.83
953		2710.65
954		2710.37

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
955		2710.10
956		2709.70
957		2709.36
958		2709.23
959		2708.75
960		2708.59
961		2707.90
962		2707.44
963		2707.04
964		2706.78
965		2706.25
966		2705.78
967		2705.19
968		2704.95
969		2704.61
970		2704.48
971		2703.94
972		2703.83
973		2703.45
974		2703.06
975		2702.76
976		2702.33
977		2701.98
978		2701.88
979		2701.80
980		2701.11
981		2700.86
982		2700.50
983		2700.34
984		2699.95
985		2699.83
986		2699.48
987		2699.28
988		2698.95
989		2698.72
990		2698.46
991		2698.05
992		2697.79
993		2697.23
994		2696.99
995		2696.76
996		2696.60
997		2696.09

TABLE 2
Continued

Line Number	Identification	Frequency Cm^{-1}
998		2696.07
999		2695.60
1000		2695.23
1001		2694.70
1002		2694.37
1003		2694.16
1004		2693.55
1005		2693.43
1006		2692.93
1007		2692.64
1008		2692.30
1009		2692.11
1010		2691.80
1011		2691.47
1012		2690.94
1013		2690.55
1014		2690.10
1015		2689.44
1016		2689.21
1017		2689.00
1018		2688.26
1019		2687.97
1020		2687.64
1021		2687.09
1022		2686.61
1023		2686.16
1024		2685.91
1025		2685.60
1026		2685.42
1027		2684.96
1028		2684.44
1029		2684.15
1030		2683.82
1031		2683.36
1032		2683.10
1033		2682.85
1034		2882.18
1035		2681.58
1036		2681.25
1037		2680.75
1038		2680.48
1039		2679.63
1040		2679.26

TABLE 2

Continued

Line Number	Identification	Frequency cm^{-1}
1041		2678.72
1042		2678.49
1043		2678.03
1044		2677.67
1045		2676.78
1046		2676.34
1047		2675.76
1048		2675.53
1049		2675.32
1050		2674.86
1051		2674.17
1052		2673.73
1053		2673.33
1054		2672.89
1055		2672.29
1056		2671.80
1057		2671.60
1058		2671.47
1059		2670.99
1060		2670.40
1061		2669.71
1062		2669.33
1063		2669.11
1064		2668.86
1065		2668.62
1066		2668.06
1067		2667.91
1068		2667.70
1069		2667.57
1070		2667.45
1071		2667.15
1072		2666.98
1073		2666.63
1074		2666.31
1075		2665.72
1076		2665.32
1077		2664.62
1078		2663.90
1079		2663.52
1080		2663.16
1081		2662.59
1082		2662.13
1083		2661.33

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
1084		2660.79
1085		2660.60
1086		2660.45
1087		2659.99
1088		2659.87
1089		2659.63
1090		2659.39
1091		2659.25
1092		2658.97
1093		2658.82
1094		2658.42
1095		2658.04
1096		2657.16
1097		2656.93
1098		2656.42
1099		2655.97
1100		2655.59
1101		2655.23
1102		2654.69
1103		2654.40
1104		2654.14
1105		2653.59
1106		2653.33
1107		2652.94
1108		2652.81
1109		2652.30
1110		2652.09
1111		2651.83
1112		2651.53
1113		2651.34
1114		2651.12
1115		2651.02
1116		2650.25
1117		2649.88
1118		2649.45
1119		2648.90
1120		2648.14
1121		2648.54
1122		2646.77
1123		2646.47
1124		2645.22
1125		2644.72
1126		2644.06

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
1127		2643.39
1128		2642.91
1129		2642.83
1130		2642.29
1131		2641.62
1132		2641.23
1133		2640.56
1134		2640.04
1135		2639.26
1136		2638.91
1137		2638.43
1138		2638.21
1139		2637.50
1140		2636.95
1141		2636.65
1142		2636.04
1143		2635.89
1144		2635.17
1145		2634.56
1146		2633.65
1147		2633.38
1148		2632.93
1149		2632.25
1150		2631.87
1151		2631.27
1152		2631.05
1153		2630.53
1154		2630.00
1155		2629.39
1156		2629.09
1157		2628.80
1158		2627.81
1159		2627.70
1160		2626.87
1161		2626.56
1162		2625.42
1163		2624.69
1164		2624.29
1165		2623.25
1166		2622.44
1167		2622.08
1168		2620.98
1169		2620.60

TABLE 2

Continued

Line Number	Identification	Frequency Cm^{-1}
1170		2620.24
1171		2619.89
1172		2618.87
1173		2618.45
1174		2618.07
1175		2617.67
1176		2615.96
1177		2615.45
1178		2614.38
1179		2613.82
1180		2613.26
1181		2612.89
1182		2612.66
1183		2611.97
1184		2611.61
1185		2611.07
1186		2610.76
1187		2609.37
1188		2609.03
1189		2607.80
1190		2606.79
1191		2606.37
1192		2605.64
1193		2604.62
1194		2603.42
1195		2602.95
1196		2602.36
1197		2601.26
1198		2599.53
1199		2597.65
1200		2595.95
1201		2592.24
1202		2591.94
1203		2590.94
1204		2589.70
1205		2588.98
1206		2588.52
1207		2587.58
1208		2586.78
1209		2584.76
1210		2583.96
1211		2583.51
1212		2582.50

TABLE 2

Continued

Line Number	Identification	Frequency Cm ⁻¹
1213		2580.92
1214		2579.69
1215		2577.35
1216		2576.86
1217		2575.22
1218		2573.91
1219		2572.58
1220		2571.87
1221		2570.96
1222		2570.34
1223		2567.91
1224		2566.72
1225		2565.94
1226		2564.97
1227		2564.67
1228		2563.14
1229		2562.17
1230		2560.33
1231		2559.64
1232		2558.94
1233		2558.27
1234		2557.35
1235		2556.00
1236		2554.89
1237		2554.07
1238		2552.70
1239		2552.32
1240		2551.81
1241		2549.95
1242		2547.42
1243		2546.51
1244		2543.16
1245		2540.34
1246		2537.93
1247		2536.32
1248		2534.05

TABLE 3
The 5.7 Micron Region Line Frequencies

Line Number	Identification	Frequency Cm^{-1}
1		1815.51
2		1814.79
3		1813.54
4		1813.01
5		1812.29
6		1811.43
7		1810.58
8		1809.28
9		1808.22
10		1807.34
11		1806.61
12		1805.77
13		1805.36
14		1804.90
15		1803.62
16		1803.06
17		1801.67
18		1801.34
19		1800.70
20	R(23)	1799.96
21		1799.57
22		1798.36
23	R(22)	1797.59
24		1796.37
25	R(21)	1795.53
26		1794.56
27		1794.10
28	R(20)	1793.48
29		1792.67
30		1791.81
31	R(19)	1791.31
32		1790.75
33		1789.68
34	R(18)	1789.15
35		1788.80
36		1787.57
37	R(17)	1787.06
38		1785.65
39	R(16)	1785.07
40		1783.49
41	R(15)	1782.89
42		1781.33

TABLE 3

Continued

Line Number	Identification	Frequency Cm ⁻¹
43	R(14)	1780.70
44		1779.08
45	R(13)	1778.41
46		1777.32
47		1776.88
48	R(12)	1776.19
49		1775.36
50	12 ₋₁₀ - 11 ₋₉	1774.76
51	R(11)	1774.01
52		1773.29
53		1772.60
54	R(10)	1771.77
55		1771.32
56	11 ₋₁₀ - 10 ₋₉	1770.63
57	10 ₋₈ - 9 ₋₇	1770.15
58	R(9)	1769.55
59	10 ₋₉ - 9 ₋₈	1768.51
60	9 ₋₇ - 8 ₋₆	1767.89
61	R(8)	1767.25
62	9 ₋₈ - 8 ₋₇	1766.36
63	8 ₋₆ - 7 ₋₅	1765.49
64	R(7)	1764.94
65	8 ₋₇ - 7 ₋₆	1764.18
66	7 ₋₅ - 6 ₋₄	1763.14
67	R(6)	1762.62
68	7 ₋₆ - 6 ₋₅	1761.96
69	6 ₋₄ - 5 ₋₃	1760.73
70	R(5)	1760.32
71	6 ₋₅ - 5 ₋₄	1759.78
72	5 ₋₃ - 4 ₋₂	1758.31
73	R(4)	1758.01
74	5 ₋₄ - 4 ₋₃	1757.58
75		1756.86
76		1755.64
77		1753.27
78		1751.43
79		1750.08
80		1748.57
81		1747.56
82		1746.99
83		1745.70
84		1741.17
85		1739.79
86		1738.84

TABLE 3

Continued

Line Number	Identification	Frequency cm^{-1}
87		1738.56
88		1736.22
89		1734.75
90	4-3 - 5-4	1734.19
91	P(5)	1733.75
92	4-2 - 5-3	1733.39
93	5-4 - 6-5	1731.75
94	P(6)	1731.22
95	5-3 - 6-4	1730.86
96		1730.00
97	6-5 - 7-6	1729.26
98	P(7)	1728.72
99	6-4 - 7-5	1728.17
100		1727.41
101	7-6 - 8-7	1726.81
102	P(8)	1726.19
103	7-5 - 8-6	1725.61
104	8-7 - 9-8	1724.35
105	P(9)	1723.63
106	8-6 - 9-7	1722.96
107	9-8 - 10-9	1721.85
108	P(10)	1721.07
109	9-7 - 10-8	1720.34
110	10-9 - 11-10	1719.42
111	P(11)	1718.47
112	10-8 - 11-9	1717.64
113	11-10 - 12-11	1716.85
114		1716.32
115	P(12)	1715.87
116	11-9 - 12-10	1715.21
117		1714.39
118		1713.94
119	P(13)	1713.21
120		1712.52
121		1711.87
122		1711.48
123	P(14)	1710.57
124		1709.83
125		1709.30
126	P(15)	1707.91
127		1707.19
128		1706.77

TABLE 3

Continued

Line Number	Identification	Frequency Cm^{-1}
129		1706.42
130	P(16)	1705.23
131		1704.51
132	P(17)	1702.57
133		1702.43
134		1700.72
135	P(18)	1699.88
136		1699.05
137	P(19)	1697.18
138		1696.53
139		1696.00
140		1695.46
141	P(20)	1694.39
142		1693.82
143		1693.10
144		1692.20
145	P(21)	1691.60
146		1691.12
147		1690.24
148		1689.55
149		1688.70
150		1687.54
151		1686.86
152	P(23)	1686.01
153		1685.21
154		1684.87
155		1684.04
156	P(24)	1683.25
157		1682.28
158		1681.27
159	P(25)	1680.52
160		1679.35
161	P(26)	1677.77
162		1676.36
163		1675.12
164		1673.48
165		1672.68
166		1668.43
167		1667.78
168		1666.85
169		1665.68

TABLE 4
The 6.7 Micron Region Line Frequencies

Line Number	Identification	Frequency Cm ⁻¹
1		1568.84
2		1568.38
3		1567.48
4		1566.99
5		1566.41
6		1565.87
7		1565.33
8		1564.82
9		1564.13
10		1563.56
11		1562.96
12		1561.79
13		1561.22
14		1560.67
15		1560.24
16		1559.68
17		1559.19
18		1558.46
19		1557.52
20		1556.52
21		1556.00
22		1554.95
23		1554.32
24		1553.69
25		1553.14
26		1552.21
27		1551.24
28		1550.98
29		1550.20
30		1549.64
31		1549.26
32		1548.74
33		1547.08
34		1546.41
35		1545.63
36		1545.12
37		1544.41
38		1543.85
39	R(16)	1543.51
40		1541.97
41		1541.23
42	R(15)	1540.93
43		1540.22
44		1539.71

TABLE 4

Continued

Line Number	Identification	Frequency cm^{-1}
45		1539.00
46	R(14)	1538.32
47		1537.39
48		1536.60
49		1536.18
50	R(13)	1535.75
51		1535.06
52		1533.85
53		1533.58
54	R(12)	1533.19
55		1532.91
56		1532.45
57		1532.19
58		1532.11
59		1531.01
60	R(11)	1530.57
61		1529.90
62		1528.90
63		1528.32
64	R(10)	1528.03
65		1527.31
66		1526.38
67		1525.92
68	$11_{-10} - 10_{-9}, 10_{-8} - 9_{-7}$	
69	R(9)	1525.46
70		1524.96
71	$10_{-9} - 9_{-8}$	1523.67
72	$9_{-7} - 8_{-6}$	1523.28
73	R(18)	1522.91
74		1522.65
75		1521.91
76		1521.26
77	$9_{-8} - 8_{-7}$	
78	$8_{-6} - 7_{-5}$	1520.66
79	R(7)	1520.35
80		1520.14
81		1519.54
82		1518.92
83	$8_{-7} - 7_{-6}$	
84	$7_{-5} - 6_{-4}, R(6)$	1517.93
85		1517.42
	$7_{-6} - 6_{-5}$	1516.65
		1516.27

TABLE 4

Continued

Line Number	Identification	Frequency cm^{-1}
86	$6_4 - 5_3, R(5)$	1515.40
87		1514.96
88	$6_5 - 6_4$	1514.27
89	$5_3 - 4_2, R(4)$	1512.90
90		1512.25
91	$5_4 - 4_3$	1511.95
92	$4_2 - 3_1, R(3)$	1510.40
93	$4_3 - 3_2$	1509.60
94		1508.51
95		1507.77
96		1507.31
97		1507.04
98		1506.55
99		1505.96
100		1505.55
101		1504.92
102		1503.93
103		1503.18
104		1502.26
105		1501.78
106		1501.08
107		1500.78
108		1500.38
109		1499.76
110		1499.33
111		1498.30
112		1497.78
113		1496.20
114		1495.47
115		1495.21
116		1494.37
117	$P(3)$	1493.09
118		1492.73
119		1491.38
120	$P(4)$	1490.81
121		1490.27
122		1489.82
123		1488.99
124	$4_3 - 5_4, P(5)$	1488.48
125	$4_2 - 5_3$	1487.79
126		1487.25

TABLE 4

Continued

Line Number	Identification	Frequency cm^{-1}
127	5-4 - 6-5, P(6)	1486.15
128		1485.87
129	5-3 - 6-4	1485.36
130		1484.73
131	6-5 - 7-6, P(7)	1484.24
132		1483.79
133	6-4 - 7-5	1483.48
134		1482.95
135	7-6 - 8-7, P(8)	1482.37
136		1481.85
137	7-5 - 8-6	1481.43
138		1480.53
139	8-7 - 9-8, P(9)	1480.62
140		1479.45
141	8-6 - 9-7	1479.10
142		1478.76
143	9-8 - 10-9, P(10)	1478.15
144		1477.66
145	9-7 - 10-8	1476.72
146		1476.45
147	10-9 - 11-10, P(11)	1476.11
148		1475.79
149	10-8 - 11-9	1475.36
150		1474.42
151	11-10 - 12-11, P(12)	1473.79
152		1473.44
153	11-9 - 12-10	1473.05
154		1471.98
155	P(14)	1471.45
156		1471.09
157	P(15)	1470.75
158		1469.86
159		1469.63
160		1469.09
161		1468.79
162		1468.46
163		1467.82
164		1467.47
165		1467.03
166		1466.74
167		1465.61
168		1465.06
169		1464.26

TABLE 4

Continued

Line Number	Identification	Frequency cm^{-1}
170		1463.99
171		1463.48
172	P(16)	1462.80
173		1461.93
174		1461.71
175	P(17)	1460.52
176		1459.68
177		1459.31
178	P(18)	1458.24
179		1457.41
180		1456.96
181		1456.47
182	P(19)	1455.94
183		1455.20
184		1454.84
185		1454.59
186		1454.10
187	P(20)	1453.70
188		1452.95
189		1452.70
190		1451.98
191	P(21)	1451.46
192		1450.77
193		1450.52
194		1450.10
195		1449.71
196		1449.33
197		1449.12
198		1448.57
199		1448.34
200		1447.90
201		1447.16
202		1446.76
203		1446.38
204		1446.16
205		1444.97
206		1444.51
207		1444.20
208		1443.93
209		1443.04
210		1442.68
211		1442.24
212		1441.76

TABLE 4
Continued

Line Number	Identification	Frequency Cm^{-1}
213		1440.46
214		1439.85
215		1439.62
216		1438.34
217		1437.92
218		1437.52
219		1436.78
220		1436.45
221		1435.70
222		1435.26
223		1434.19
224		1433.61
225		1433.16
226		1432.87
227		1432.35
228		1432.01
229		1431.43
230		1431.01
231		1430.45
232		1429.91
233		1429.00
234		1428.82
235		1428.27

TABLE 5

The 7.5 to 10 Micron Region Line Frequencies*

Line Number	Identification	Frequency Cm^{-1}
1		1426.27
2		1425.91
3		1424.77
4		1424.26
5		1423.68
6		1422.51
7		1422.12
8		1420.23
9	$R_{R_5'}(20)$	1420.01
10		1419.46
11		1418.97
12	$R_{R_5'}(19)$	1417.90
13		1417.50
14		1417.21
15		1416.68
16	$R_{R_5'}(18)$	1415.71
17	$R_{R_5'}(17)$	1413.48
18	$R_{R_5'}(16)$	1411.36
19	$R_{R_5'}(15)$	1409.16
20	$R_{R_5'}(14)$	1406.94
21		1404.98
22		1404.73
23	$R_{R_5'}(13)$	1402.82
24	$R_{R_5'}(12)$	1402.43
25	$R_{R_5'}(11)$	1400.26
26		1399.19
27	$R_{R_5'}(10)$	1397.97
28	$R_{R_5'}(9)$	1395.72
29		1394.47
30		1393.79
31	$R_{R_5'}(8)$	1393.36
32		1391.59
33	$R_{R_5'}(7)$	1391.04
34		1390.23
35		1389.43
36	$R_{R_5'}(6)$	1388.69
37		1387.49
38		1387.23

* The primed terms refer to the ν_5 band while the unprimed terms refer to the ν_6 band.

TABLE 5.

Continued

Line Number	Identification	Frequency cm^{-1}
39	$\text{RR}_5^1(5)$	1386.35
40		1384.97
41		1382.78
42		1382.30
43		1380.50
44		1379.77
45		1378.71
46		1378.16
47		1377.49
48		1376.59
49		1375.93
50		1375.08
51		1373.73
52		1372.76
53		1372.32
54		1371.55
55		1371.34
56		1370.60
57		1370.00
58		1368.95
59		1368.64
60		1368.17
61		1366.96
62		1366.68
63		1365.87
64		1365.00
65		1364.29
66		1363.50
67		1363.09
68		1362.59
69		1361.94
70		1361.06
71		1359.57
72		1358.98
73		1358.77
74	$\text{RR}_3^1(13)$	1356.63
75	$\text{RR}_3^1(12)$	1354.37
76	$\text{RR}_3^1(11)$	1352.11
77	$\text{RR}_3^1(10)$	1349.79
78	$\text{RR}_3^1(9)$	1348.80
79		1347.38
80		1346.13

TABLE 5

Continued

Line Number	Identification	Frequency Cm^{-1}
81	$R_{R\frac{1}{2}}(8)$	1345.15
82	$R_{R\frac{1}{2}}(7)$	1342.79
83	$R_{R\frac{1}{2}}(6)$	1340.39
84		1339.57
85		1339.08
86		1338.56
87	$R_{R\frac{1}{2}}(5)$	1337.98
88		1337.48
89		1336.66
90		1336.20
91	$R_{R\frac{1}{2}}(4)$	1335.66
92		1334.81
93		1334.25
94	$R_{R\frac{1}{2}}(3)$	1333.28
95		1332.79
96		1332.15
97		1331.65
98		1331.19
99		1330.37
100		1329.79
101		1328.99
102		1327.92
103		1327.58
104		1327.11
105		1326.31
106		1325.95
107		1325.43
108		1324.71
109		1323.90
110		1323.31
111		1322.43
112		1322.18
113		1321.78
114		1321.32
115		1320.93
116		1320.38
117		1319.65
118		1319.04
119		1318.22
120		1317.76
121		1217.28
122		1316.97

TABLE 5
Continued

Line Number	Identification	Frequency Cm^{-1}
123		1316.06
124		1315.14
125		1314.92
126		1314.44
127		1313.85
128		1313.49
129		1312.83
130		1312.54
131		1311.94
132		1311.31
133		1311.10
134		1310.07
135		1309.84
136		1309.53
137		1308.94
138		1308.39
139		1307.71
140		1307.42
141		1307.00
142		1306.36
143		1305.47
144		1303.52
145		1303.94
146		1303.37
147		1302.39
148		1302.19
149		1301.73
150		1301.37
151		1300.69
152		1300.42
153		1299.70
154		1299.16
155		1298.39
156		1297.80
157	$7'_{-3} - 6'_{-5}$	1297.44
158		1296.11
159		1296.32
160		1295.61
161		1295.08
162		1294.71
163	$6'_{-2} - 5'_{-4}$	1294.48
164	$7'_{-4} - 6'_{-4}$	

TABLE 5

Continued

Line Number	Identification	Frequency Cm^{-1}
165		1293.46
166		1292.21
167	$6'-3 - 5'-3$	1291.89
168	$5'-1 - 4'-3$	1291.54
169	$5'-2 - 4'-2$	1289.94
170		1289.64
171	$4'-0 - 3'-2$	1288.69
172		1288.32
173	$4'-1 - 3'-1$	1287.73
174		1287.29
175		1287.06
176		1286.06
177		1285.70
178		1284.91
179		1284.40
180		1283.93
181		1283.49
182		1283.01
183		1282.15
184		1281.70
185		1281.48
186	$7'-4 - 7'-6$	1280.79
187	$6'-3 - 6'-5$	1280.29
188	$5'-2 - 5'-4$	1279.75
189	$4'-1 - 4'-3$	1279.34
190	$3'-0 - 3'-2$	1278.94
191	$2'-2 - 2'-0$	1278.14
192	$3'-1 - 3'-1$	1277.79
193	$5'-1 - 5'-3, 4'-0 - 4'-2$	1277.49
194	$6'-2 - 6'-4$	1276.97
195	$7'-3 - 7'-5$	1276.54
196		1276.16
197		1275.66
198		1275.07
199		1274.53
200		1274.23
201	$12'-12 - 11'-10$	1273.38
202		1271.75
203		1271.20
204		1270.25
205		1269.83

TABLE 5

Continued

Line Number	Identification	Frequency Cm^{-1}
206	$3'-0 - 4'-2$	1269.44
207	$3'-1 - 4'-3$	1268.06
208	$10'-10 - 9'-8$	1267.75
209		1266.44
210	$5'-1 - 6'-5$	1265.79
211	$4'-0 - 5'-4$	1265.24
212	$9'-9 - 8'-7$	1264.92
213	$6'-2 - 7'-6$	1263.83
214		1263.19
215		1262.76
216	$5'-2-6'-4, 7'-3-8'-7$	1262.31
217	$8'-8 - 7'-6$	1262.07
218		1261.83
219		1260.95
220		1260.35
221		1259.80
222	$7'-7-6'-5, 6'-3-7'-5$	1259.32
223		1258.78
224		1258.29
225		1257.37
226	$6'-6 - 5'-4$	1256.45
227		1255.80
228	$5'-5 - 4'-3$	1253.72
229		1253.12
230		1252.72
231		1252.10
232		1250.88
233		1250.20
234		1249.56
235	$3'-3 - 2'-1$	1248.34
236		1248.07
237		1246.63
238	$2'-2 - 1'-0$	1245.80
239		1245.05
240		1243.72
241		1243.43
242		1242.82
243		1242.05
244		1241.56
245	$2'-2 - 2'-0$	1240.67
246	$3'-3 - 3'-1$	1240.38
247	$4'-4 - 4'-2$	1240.04

TABLE 5

Continued

Line Number	Identification	Frequency cm^{-1}
248	5'-5 - 5'-3	1239.54
249	6'-6 - 6'-4	1239.01
250	7'-7 - 7'-5	1238.35
251	8'-8 - 8'-6	1237.52
252		1237.08
253	9'-9 - 9'-7	1236.64
254		1236.29
255	10'-10 - 10'-8	1235.54
256		1234.66
257	11'-11-11'-9, 2'-2-3'-2	1234.26
258		1233.43
259		1232.95
260	3'-3-4'-3, 12'-12-12'-10	1231.95
261		1231.41
262	4'-4 - 5'-4	1229.84
263		1228.55
264	5'-5 - 6'-5	1227.87
265		1227.21
266		1226.72
267		1226.45
268		1224.97
269	7'-7 - 8'-7	1224.03
270		1223.78
271		1223.45
272		1222.87
273	8'-8 - 9'-8	1222.22
274		1221.49
275		1220.94
276	9'-9 - 10'-9	1220.42
277		1220.17
278		1219.39
279		1219.10
280	10'-10 - 11'-10	1218.66
281		1218.25
282		1217.90
283		1217.24
284	11'-11 - 12'-11	1216.85
285		1216.56
286		1215.86
287		1215.07
288		1214.71
289		1214.39
290		1213.96
291		1213.11

TABLE 5

Continued

Line Number	Identification	Frequency Cm^{-1}
292		1212.58
293		1211.79
294		1211.40
295		1210.98
296		1210.51
297		1209.79
298		1209.54
299		1208.86
300		1208.09
301		1207.64
302		1207.01
303		1206.39
304		1205.79
305		1205.12
306		1204.63
307		1204.12
308		1203.73
309		1203.43
310		1202.89
311		1202.04
312		1201.79
313		1200.93
314		1200.46
315		1199.79
316		1198.92
317		1198.50
318		1197.63
319		1197.20
320		1196.02
321		1195.61
322		1194.19
323		1193.83
324		1193.53
325		1192.60
326		1192.10
327		1191.60
328		1191.04
329		1190.62
330		1190.13
331		1189.29
332		1188.38
333		1187.76
334		1187.05
335		1185.83
336		1185.28

TABLE 5

Continued

Line Number	Identification	Frequency Cm ⁻¹
337		1184.79
338		1184.42
339		1183.33
340		1182.65
341		1182.25
342		1182.12
343		1181.77
344		1181.16
345		1180.74
346	12 ₋₁₂ - 11 ₋₉	1180.40
347		1179.79
348	11 ₋₁₁ - 10 ₋₈	1179.39
349		1178.70
350	10 ₋₁₀ - 9 ₋₇	1178.24
351		1177.93
352		1177.87
353	9 ₋₉ - 8 ₋₆	1176.87
354		1186.21
355		1175.94
356		1175.65
357	8 ₋₈ - 7 ₋₆	1175.44
358		1175.04
359	7 ₋₇ - 6 ₋₄	1173.79
360		1173.23
361		1172.89
362		1172.39
363	6 ₋₆ - 5 ₋₃	1172.07
364		1171.54
363		1171.00
366		1170.42
367	5 ₋₅ - 4 ₋₂	1169.97
368		1169.51
369		1168.94
370	4 ₋₄ - 3 ₋₁	1168.22
371		1167.72
372		1167.37
373		1166.94
374		1166.36
375		1165.85
376		1165.30
377		1165.12
378		1164.93
379		1164.71
380		1164.25
381		1163.91

TABLE 5

Continued

Line Number	Identification	Frequency Cm^{-1}
382		1163.59
383		1163.27
384	12 ₋₁₂ - 12 ₋₁₁	1162.91
385	11 ₋₁₁ - 11 ₋₁₀	1162.48
386	10 ₋₁₀ - 10 ₋₉	1162.07
387	9 ₋₉ - 9 ₋₈	1161.66
388	8 ₋₈ - 8 ₋₇	1161.20
389	7 ₋₇ - 7 ₋₆	1160.80
390	6 ₋₆ - 6 ₋₅	1160.42
391	5 ₋₅ - 5 ₋₄	1160.04
392	4 ₋₄ - 4 ₋₃	1159.72
393		1159.37
394		1158.46
395		1158.11
396		1156.72
397		1155.83
398		1154.93
399		1154.39
400		1153.83
401		1153.30
402		1153.02
403		1152.31
404		1151.86
405	2 ₋₂ - 3 ₋₁	1151.09
406		1150.56
407		1149.90
408		1149.45
409		1149.04
410	3 ₋₃ - 4 ₋₂	1148.43
411		1147.75
412		1146.92
413		1146.42
414	4 ₋₄ - 5 ₋₃	1145.64
415		1145.09
416		1144.54
417		1143.97
418		1143.16
419	5 ₋₅ - 6 ₋₄	1142.54
420		1140.65
421		1140.05
422	6 ₋₆ - 7 ₋₅	1139.46
423		1138.87
424		1137.97
425		1136.54

TABLE 5

Continued

Line Number	Identification	Frequency cm^{-1}
426	7-7 - 8-6	1136.25
427		1135.65
428		1134.23
429	8-8 - 9-7	1133.33
430		1132.90
431		1132.41
432		1131.42
433		1130.48
434	9-9 - 10-8	1129.46
435		1128.53
436		1127.59
437		1126.74
438	10-10 - 11-9	1125.82
439		1125.13
440		1124.37
441		1123.69
442		1123.11
443	11-11 - 12-10	1122.63
444		1121.92
445		1121.15
446		1120.02
447		1119.65
448		1119.21
449		1118.64
450		1118.05
451		1117.31
452		1116.35
453	$\text{P}_{\text{P}_3}(3)$	1115.28
454		1113.91
455		1113.40
456	$\text{P}_{\text{P}_3}(4)$	1113.12
457		1112.60
458		1111.44
459	$\text{P}_{\text{P}_3}(5)$	1110.89
460		1109.71
461		1109.00
462	$\text{P}_{\text{P}_3}(6)$	1106.54
463		1105.89
464		1105.37
465	$\text{P}_{\text{P}_3}(7)$	1105.02
466		1104.45
467		1104.06
468		1103.42
469		1102.65
470		1102.04

TABLE 5

Continued

Line Number	Identification	Frequency cm^{-1}
471	$\text{Pp}_3(8)$	1101.58
472		1100.93
473	$\text{Pp}_3(9)$	1099.83
474		1098.90
475		1098.55
476	$\text{Pp}_3(10)$	1096.90
477		1096.23
478		1095.13
479	$\text{Pp}_3(11)$	1094.60
480		1093.53
481		1092.34
482	$\text{Pp}_3(12)$	1091.53
483		1090.89
484		1090.02
485		1089.52
486		1087.99
487		1087.00
488		1085.75
489		1085.26
490		1084.56
491		1082.60
492		1082.39
493		1082.08
494		1080.56
495		1079.50
496		1077.09
497		1076.42
498		1075.70
499		1075.17
500		1074.09
501		1073.39
502		1073.04
503		1072.55
504		1072.05
505		1070.76
506		1070.06
507		1069.49
508		1068.38
509		1066.93
510		1065.81
511		1065.17
512		1064.45
513	$\text{Pp}_5(5)$	1063.49
514		1061.99
515	$\text{Pp}_5(6)$	1061.33

TABLE 5

Continued

Line Number	Identification	Frequency Cm^{-1}
516		1060.50
517		1059.11
518	$\text{P}_{\text{P}_5}(7)$	1058.84
519	$\text{P}_{\text{P}_5}(8)$	1056.36
520	$\text{P}_{\text{P}_5}(9)$	1053.80
521	$\text{P}_{\text{P}_5}(10)$	1051.27
522	$\text{P}_{\text{P}_5}(11)$	1048.76
523	$\text{P}_{\text{P}_5}(12)$	1046.21
524	$\text{P}_{\text{P}_5}(13)$	1043.62
525	$\text{P}_{\text{P}_5}(14)$	1040.99
526	$\text{P}_{\text{P}_5}(15)$	1038.40
527		1037.69
528		1037.18
529		1035.76
530		1033.94
531		1033.19
532		1032.23
533		1030.66
534		1029.72
535		1028.03
536		1037.38
537		1026.90
538		1026.74
539		1025.59
540		1024.77
541		1023.64
542		1022.75
543		1022.29
544		1021.83
545		1019.87
546		1019.75
547		1017.39
548		1014.82
549		1014.37
550	$\text{P}_{\text{P}_7}(7)$	1009.66
551		1009.37
552	$\text{P}_{\text{P}_7}(8)$	1007.65
553	$\text{P}_{\text{P}_7}(9)$	1005.16
554	$\text{P}_{\text{P}_7}(10)$	1002.65
555		1001.12
556	$\text{P}_{\text{P}_7}(11)$	1000.19

TABLE 5

Continued

Line Number	Identification	Frequency Cm^{-1}
557	$\text{P}_{\text{P}7}(12)$	997.69
558	$\text{P}_{\text{P}7}(13)$	995.20
559	$\text{P}_{\text{P}7}(14)$	992.68
560	$\text{P}_{\text{P}7}(15)$	990.17
562	$\text{P}_{\text{P}7}(16)$	987.73
563	$\text{P}_{\text{P}7}(17)$	985.17
564	$\text{P}_{\text{P}7}(18)$	982.67
565	$\text{P}_{\text{P}7}(19)$	980.18
566	$\text{P}_{\text{P}7}(20)$	977.67
567		976.63
568		974.97
569		972.66

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