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James Alexander Coakley, Jr.
(Ph.D. Thesis)

September 1972

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RADIATIVE TRANSFER IN A DENSE WATER VAPOR ATMOSPHERE

Contents

Abstract ........................................ iii
I. Introduction .................................. 1
II. The Approximate Mean Absorption Coefficient of Water Vapor at High Pressures .......... 4
III. The Mean Absorption Coefficient of H2O .... 35
IV. Radiative Transfer in a Dense Water Vapor Atmosphere .................................. 39
V. Thermal Radiative Flux for Pure Water Vapor Atmospheres .................................. 52
VI. Summary ...................................... 57
Acknowledgements ................................ 60
References ....................................... 61
RADIATIVE TRANSFER IN A DENSE WATER VAPOR ATMOSPHERE

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September 1972

ABSTRACT

An approximate mean absorption coefficient was obtained for the pure rotation spectrum of H$_2$O from the Fourier transform of the molecular dipole autocorrelation function. The correlation function was calculated from a classical description of the molecule's rotation. The expression for the absorption coefficient was parameterized so that the temperature dependence of the coefficient could be easily obtained. When a comparison was made between the results of these classical calculations of the absorption coefficient and those of quantum mechanics, it was found that the classical values were significantly lower than the quantum mechanical values of the mean absorption coefficient. It was suggested that a correction could be made to the classical method which would improve the agreement between the classical and the quantum mechanical absorption coefficients. It was shown that the results given for the pure rotation spectrum could be generalized to the vibration-rotation bands as well. In this manner the mean absorp-
tion coefficient of H$_2$O was obtained for use in planetary radiative transfer calculations. The calculations of the thermal radiative flux was performed for several pure water vapor atmospheres. A comparison was made between a gray and a nongray calculation of the flux for the water vapor atmosphere which would have formed if the oceans had been evaporated. Due to the fact that the mean absorption coefficient allows for window regions between the absorption bands, the radiative flux emitted by the nongray atmosphere was much larger than that for the gray atmosphere with a similar temperature profile. Furthermore, the lower regions of the nongray atmosphere were convectively unstable while those of the corresponding gray atmosphere were not. Finally, the radiative flux was obtained for planets with pure water vapor atmospheres having a constant relative humidity in their tropospheres. The calculations were performed for 25% and 100% relative humidity and for several values of the surface temperature. It was observed that the thermal radiative flux emitted by a low pressure planetary atmosphere was underestimated when the mean absorption coefficient was used to describe the atmospheric absorption spectrum.
INTRODUCTION

The moon is presently receding from the earth. The recession is apparently due to tidal friction. When the past orbit of the moon is calculated using the present rate of recession, taking into account the effect of the ocean tides, it is found that the moon was within a few earth radii of the earth between one and two billion years ago. Walter Munk in his Harold Jeffreys Lecture, "Once Again--Tidal Friction," described the considerations which led to this conclusion. He went even further. When the moon was close to the earth--he presented calculations for the cases when the moon was within 6 and 2.89 earth radii--Munk calculated that the energy dissipated in the tides was orders of magnitude greater than the amount needed to vaporize the oceans. If the oceans had been evaporated, the resulting atmosphere would have been a water vapor atmosphere having the weight of the oceans. Assuming this atmosphere to be a gray absorber--the absorption spectrum is independent of frequency--Munk calculated that only a moderate value of dissipation due to atmospheric friction within a boundary layer at the surface of the earth was needed to maintain surface temperatures greater than 1000°K. He suggested that if
the true absorption spectrum of water vapor were used in these calculations such high surface temperatures would probably not have been obtained.

An improvement of Munk's calculations was sought by introducing a representative spectrum for the infrared absorption due to water vapor into the radiative transfer calculations. It was hoped that a better understanding would be obtained of the magnitude of the radiative flux necessary to maintain a high surface temperature on a planet having such a heavy water vapor atmosphere. Furthermore, the nongray calculations could be used to illuminate the limitations of a gray approximation to a nongray absorption spectrum.

First it was necessary to describe the absorption in the infrared due to water vapor. Most of the radiation coming from a planetary surface is in the infrared. At the high pressures encountered in the heavy water vapor atmosphere the rotational absorption lines would overlap each other. Therefore, it is possible to describe the appropriate absorption coefficient at a given wavenumber in terms of a local mean absorption coefficient. The mean absorption coefficient for H₂O was obtained as described in the next section. It was used in a nongray analogue to Munk's gray calculations. A comparison of the results
are given in Section IV.

Further applications of the mean absorption coefficients to radiative transfer problems were made. The thermal radiative flux emitted by various pure water vapor planetary atmospheres was calculated. The atmospheres were assumed to have a constant relative humidity in their tropospheres. The calculations were performed for 25% and 100% relative humidities and for several planetary surface temperatures. A comparison was made between the results obtained using the mean absorption coefficient and those obtained by Pollack\(^2\) for similar calculations using a different model for the absorption due to water vapor. These results are presented in Section V.
THE APPROXIMATE MEAN ABSORPTION COEFFICIENT OF 
WATER VAPOR AT HIGH PRESSURES

At pressures high enough to cause the rotational 
lines of an absorption spectrum to overlap, a mean absorption 
coefficient may be calculated using a just-overlapping 
line (JOL) model. Tejwani and Varanasi used data on 
line strengths and positions in a JOL model to estimate 
the mean absorption coefficients of the short wavelength 
region of the water vapor rotation band at several tempera­
tures. Ludwig et al approximated the mean coefficient 
in the short wavelength region of the water vapor rotation 
band by using a weighted mean of the absorption coefficients 
of a symmetric top and a "most asymmetric" top molecule 
calculated with a JOL model. Earlier, Thomson estimated 
the mean absorption coefficients of water vapor by computing 
the coefficient of a "nearly symmetric" top with the 
JOL model. It was felt that these methods of calculation 
were not appropriate for radiative transfer calculations. 
Owing to the large number of lines in the H₂O spectrum 
and to the large variety of lower state energy levels 
among neighboring lines, an impractically large number 
of calculations is required to determine the temperature 
dependence of the mean absorption coefficient evaluated
by the method Tejwani and Varanasi used. Furthermore, the calculation of the absorption of an asymmetric molecule from symmetric top models will be in error—and at least in theory. Consequently, another method of calculating the absorption coefficient was sought which would facilitate the determination of the temperature dependence of the coefficient for radiative transfer calculations and at the same time would not suffer from the objections of being based on a model for a molecule other than an asymmetric rotor. The calculations presented here are based entirely on the dynamics of an asymmetric top similar to the water molecule. The results offer a method for easily estimating the absorption coefficient at any temperature.

The mean absorption coefficient of the pure rotation spectrum of an asymmetric rotor similar to H₂O was calculated. It is compared with the coefficient computed from quantum mechanics. A method is also given for generalizing the results to the vibration-rotation bands.

The method used to calculate the mean absorption coefficient is described by Gordon. The absorption coefficient (in atm⁻¹cm⁻¹) is given by

\[ k_\nu (r) = \frac{8\pi^3}{3\hbar c} \frac{N_o T_0}{T} \nu (1 - e^{-\frac{h\nu}{kT}}) \varphi (\nu) \]  

(1)
$N_0$ is the number of absorbing molecules per unit volume at the temperature $T_0$ and one atmosphere; $h$ is Plank's constant; $T$ is the temperature of the gas; $K$ is Boltzmann's constant; $c$ is the speed of light; and $\nu$ is the frequency (in cm$^{-1}$). $\mathcal{P}(\nu)$, the power spectrum, is the Fourier transform of the autocorrelation function of the molecular dipole moment.

$$\mathcal{P}(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i\nu t} < \mathbf{\mu}(0) \cdot \mathbf{\mu}(t) >_0$$

(2)

The autocorrelation function is a function of time $t$. It is the ensemble average of the scalar product between the dipole moment of a molecule at some initial time $t_0$ and itself at some later time $t + t_0$.

In these calculations the autocorrelation function was calculated assuming the molecule moved according to the laws of classical mechanics. Classically the energy of the top can have any value. Consequently, absorption occurs over a continuous range of frequencies. This is in contrast to the discrete energy states and line absorption obtained from quantum mechanical models. The use of classical mechanics to evaluate the autocorrelation function for the purpose of computing absorption coefficients has resulted in expressions for the coefficients of linear
and symmetric top molecules identical to those obtained with the JOL model.

In computing the autocorrelation function of an asymmetric molecule the following assumptions were made. First of all the calculations were performed as if the molecule were rigid. The vibrational frequencies of the molecule were assumed to be substantially higher than the rotation frequencies. The autocorrelation function of a vibrating molecule was calculated as if the average dipole moment were rotating with the molecule. The resulting frequencies of absorption were then measured from the frequency of vibration. Secondly, it was assumed that the molecule rotates freely. The perturbations resulting from intermolecular forces and collisions which affect the line shape and position were not considered here. Since the determination of a mean coefficient equivalent to that obtained by averaging the line strengths in a frequency interval containing many lines was sought, the effect of line shapes and frequency shifts should be minor. In practice the resolution required to obtain an approximate mean absorption coefficient is so low that it is not necessary to evaluate the correlation function at times as large as the collision period where it is expected that collisions would cause considerable alterations to the function. Nevertheless, at
extremely high pressures the period between collisions becomes very short and the perturbations to the autocorrelation function are reflected as changes in the envelope of the absorption band. Finally, it was assumed that the gas was in equilibrium and the occupation of the states of the gas was given by a Boltzmann distribution.

For the classical calculation of the autocorrelation function the principal moments of inertia of the molecule were oriented on a fixed reference frame with Euler angles as in Fig. 1. The fixed Z axis is in the direction of the total angular momentum vector \( \mathbf{J} \). A, B, and C are the rotation constants (in cm\(^{-1}\)): \( A > B > C \). \( \mathbf{K} \) is the angular momentum along the body C axis of the molecule. For this orientation \( K/J = \cos \theta \).

The Hamiltonian for the rotating top is

\[
H = J^2 (A \sin^2 \psi + B \cos^2 \psi) + K^2 (C - A \sin^2 \psi - B \cos^2 \psi)
\]

\[
= J^2 (A-B)(\alpha + \sin^2 \psi) - K^2 (A-B)(\chi + \sin^2 \psi)
\]  \hspace{1cm} (3)

where \( \alpha = B/(A - B) \) and \( \chi = (B - C)/(A - B) \) have proven to be a useful parameterization of the rotation constants. The units of energy are cm\(^{-1}\) and angular momentum is dimensionless. Since the rotation is assumed to be free, both the energy and total angular momentum are conserved.
Fig. 1. Orientation of an asymmetric rotor molecule to a fixed reference frame (XYZ). The principal moments of inertia of the molecule are aligned along the corresponding ABC axis. \( \mathbf{J} \), the total angular momentum, is directed along the fixed Z axis. \( \mathbf{K} \) is the angular momentum along the body C axis.
The energy is equivalent to the Hamiltonian.

\[ E = J^2(A - B)(\alpha + X_0) \]  

(4)

where \( X_0 = \sin^2 \psi(0) - \frac{K^2(0)}{J^2}(\chi + \sin^2 \psi(0)) \).

\( \psi(0) \) and \( K(0) \) are the values of \( \psi \) and \( |\vec{k}| \) at \( t = 0 \).

The permanent dipole moment of \( \text{H}_2\text{O} \) is along the axis of the intermediate principal moment of inertia. Thus

\[
\vec{\mu}(0) \cdot \vec{\mu}(t) = \mu_B^2 \left\{ \left[ \sin \psi(0) \sin \psi(t) + \cos \psi(0) \cos \psi(t) \frac{K(0)K(t)}{J^2} \right] \cos(\phi(t) - \phi(0)) \\
+ \left[ \sin \psi(0) \cos \psi(t) \frac{K(t)}{J} - \sin \psi(t) \cos \psi(0) \frac{K(0)}{J} \sin(\phi(t) - \phi(0)) \right] \\
+ \cos \psi(0) \cos \psi(t) \left(1 - \frac{K^2(0)}{J^2}\right)^{1/2} \left(1 - \frac{K^2(t)}{J^2}\right)^{1/2} \right\}. 
\]  

(5)

The values \( \psi(0) \) and \( K(0)/J = \cos \theta(0) \) are initial conditions. \( \psi(t) \), \( K(t)/J \), and \( \phi(t) - \phi(0) \) were calculated by solving the classical equations of motion.

The solutions for \( \psi(t) \) and \( \theta(t) \) were obtained from Euler's equations relating the angular velocities.\(^8,9\)

Once the solution \( \psi(t) \) is obtained, \( \phi(t) - \phi(0) \) may be
determined. From the Hamiltonian

$$\dot{\phi} = \frac{\partial H}{\partial J} = 2J(A-B)(\alpha + \sin^2 \psi(t))$$

gives

$$\phi(t) - \phi(0) = 2J(A-B)\alpha t + \int_0^t dt' \sin^2 \psi(t').$$  \hspace{1cm} (6)

The integral in equation (6) was done numerically after a change of variables had been made.

$$E = \text{ARCSIN} \left( \frac{1-S\sin^2 \psi}{1-X_0} \right)^{1/2}$$

gives

$$\int_0^t dt' \sin^2 \psi(t') = \int_{E_0}^E \left[ \frac{1-(1-X_0)\sin^2 \psi'}{1+X -(1-X_0)\sin^2 \psi'} \right]^{1/2}$$  \hspace{1cm} (7)

where the equation of motion

$$\dot{\psi} = \frac{\partial H}{\partial K} = -2K(A-B)(\alpha + \sin^2 \psi)$$

has been used to relate $\psi$ to $t$.

The power spectrum was computed from

$$P(\nu) = \frac{1}{Q_R} \frac{1}{2\pi} \int dt' \int_0^\infty J dJ \int_{-J}^J dK_0 \int_0^\infty \left\{ \dot{\psi}(0) \cdot \dot{\psi}(t') \right\} \exp (-\theta E(J,X_0)) \exp (-i\nu t')$$  \hspace{1cm} (8)

where the expression for the autocorrelation function has been substituted in equation (2). $Q_R$ is the rotational partition function

$$Q_R = \frac{2\pi}{\theta^3} \int_0^\infty \int_0^\infty \int_{-J}^J \exp (-\theta E(J,X_0)) = 2 \left( \frac{\pi^3 \theta^3}{8^3 \Lambda B C} \right)^{1/2}.$$
E is the energy, \( \Theta \) is \( \hbar c/KT \), \( K_0 \) and \( \Theta_0 \) are the initial conditions. Equation (8) was parameterized further.

Letting
\[
\mathcal{J} = \left[ \frac{E(A-B)}{e} \right]^{1/2} J
\]
and
\[
\tau = 2 \left( \frac{A-B}{e} \right)^{1/2} t
\]
and \( K_0/J = \cos \Theta(0) = M_0 \)

equation (8) becomes
\[
\begin{align*}
\mathcal{J}(\lambda) &= \frac{1}{QR} \frac{1}{B(A-B)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} l^2 \int_{-1}^{1} \int_{0}^{2\pi} I(\lambda, \alpha, \chi) \\
&= \frac{1}{QR} \frac{\mu_B^2}{B(A-B)^2} \mathcal{J}(\lambda, \alpha, \chi)
\end{align*}
\]

where
\[
\lambda = \frac{\sqrt{2}}{Z} \left( \frac{A-B}{e} \right)^{1/2}
\]

A calculation of \( I(\lambda, \alpha, \chi) \) was performed on a CDC 7600 for \( \alpha \) and \( \chi \) representative of an \( H_2O \) molecule (see Table 1). The results of the calculation are given in Fig. 2. The calculations required nearly an hour of computer time. The integral over \( \mathcal{J} \) in equation (9) was performed first using Simpson's formula. The results of this integral represent the autocorrelation function of an
Fig. 2. $I(\lambda)$. $\alpha = 1.085 \quad \chi = .3904$
ensemble in which all of the molecules have the same initial values \( \psi_0, \phi_0 \). Next the Fourier transform was performed by a Fast-Fourier transform routine. The results of the transform represent the power spectrum of the ensemble with the initial orientation \( \psi_0, \phi_0 \).

Owing to the limited numerical accuracy of the calculations, negative numbers appeared in some of these power spectra for various \( \psi_0 \) and \( \phi_0 \). In all cases the negative components appeared in the wings of the power spectrum where the magnitude of the spectral components should have been small. As a computational procedure all negative numbers were set to zero before the calculation of the complete power spectrum was continued.

The final step in the evaluation of \( I(\lambda) \) involved the averaging of the power spectra for each \( \psi_0 \) and \( \phi_0 \) over 85 configurations of \( \psi_0 \) and \( \phi_0 \). The values of \( \psi_0 \) and \( \phi_0 \) for the calculation were chosen so that a similar evaluation of the partition function was within one percent of the correct value. Due to the negative components in the individual power spectra the results at \( \lambda = 0 \) and for large \( \lambda \) are not expected to be accurate.

The parameterization of equation (8) was chosen so that the results of the evaluation of \( I(\lambda) \) would apply to a family of molecules having the values of \( \psi \) and \( \phi \) in common.
Once $I(\lambda)$ has been determined the absorption coefficient in the rotation band of the gas at any wavenumber and temperature may be easily computed using equations (1), (10), (11) and the molecular constants $\mathcal{A}$, $A$, $B$, and $C$.

The absorption coefficient in the pure rotation band of H$_2$O was computed using (1), (10), and (11). The values of the rotation constants used in these calculations are listed in Table 1. They were determined by Hall and Dowling\textsuperscript{11} from a high resolution study of the pure rotation spectrum. The calculations were performed for a gas at 250°K, 300°K, and at 500°K. The results are shown in Figs. 3, 4, and 5. The results of quantum mechanical calculations for the same spectrum are also presented for comparison. The dipole moment in these calculations was $1.87 \times 10^{-18}$ esu.\textsuperscript{3}

### Table 1.

Values of the rotation constants (in cm$^{-1}$) for the rotation spectrum of H$_2$O

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.8761</td>
<td>14.5074</td>
<td>9.2877</td>
</tr>
</tbody>
</table>

\[ \chi = \frac{B - C}{A - B} = 0.3904 \quad \alpha = \frac{B}{A - B} = 1.085 \]

The quantum mechanical calculations were performed
Figs. 3, 4, and 5. The calculated mean absorption coefficients at 250° K, 300° K, and 500° K. The dashed lines refer to the classical calculations. The solid lines refer to the quantum mechanical calculations.
in the following manner. First the energy levels were obtained by computing the Hamiltonian matrix in the symmetric rotor representation. The matrix was diagonalized to obtain the energy eigenvalues of the asymmetric rotor. The transition matrix elements were obtained by computing the transition matrix in the symmetric rotor representation and then transforming it to the asymmetric representation using the transformation matrix which diagonalized the Hamiltonian matrix. The resulting energy levels and transition matrix elements were used to compute line strengths and transition frequencies. The mean absorption coefficient at the wavenumber \( \nu \) was calculated at every 20 cm\(^{-1} \) by averaging the strengths of the lines in a 60 cm\(^{-1} \) interval centered at \( \nu \). A smooth curve was then drawn through the points.

A similar calculation for \( \text{H}_2\text{O} \) at 500° K which includes the effects of centrifugal distortion is compared to the results for the rigid asymmetric rotor in Fig. 6. The rotational Hamiltonian used for these calculations appeared in a paper by Fraley and Rao. The distortion constants used in the calculation were those given by Hall and Dowling. It appears that the effect of centrifugal distortions is small when the mean absorption coefficient includes contributions from lines in a wide spectral interval.
Fig. 6. Comparison of the results for calculations of the absorption coefficients for the rigid rotor and for $\text{H}_2\text{O}$ taking into account the centrifugal distortions.
The absorption coefficient calculated by the classical method are significantly smaller than those calculated using quantum mechanics. This phenomena had been noticed earlier in comparisons of similar calculations of the R branch of a linear rotor vibration-rotation band. The fault of the classical calculations seemed to be the neglect of integers with respect to the total angular momentum quantum number J.

In the case of the asymmetric rotor, the failure of the classical model to provide the integers which appear in the quantum mechanical expressions for the transition matrix elements (see Ref. 13) appears to be the cause of the lower classical values. The discrepancy between the classical and the quantum calculations is greater at 250° K and 300° K than at 500° K. This can be explained by the fact that at the lower temperature the absorption is due to excitation of levels at lower angular momentum quantum numbers. As a result, the error in neglecting the integers compared with the total angular momentum quantum number becomes larger. Of course, this implies that at temperatures large enough to cause the predominant absorption to be due to states having large quantum numbers, the classical and quantum calculations should come into agreement.

The quantum mechanical calculations were repeated leaving out the integers which normally appear in the matrix
elements. As shown in Figs. 7, 8, and 9 this dramatically improved the agreement between the classical and quantum calculations.

Owing to the considerable amount of computer time required to perform the classical calculations, no attempt was made to improve the value of $I(\lambda)$ by adjusting the expression for $\tilde{\mu}(0) \cdot \tilde{\mu}(t)$. The corrections required to improve the agreement between these classical calculations and the quantum mechanical calculations should be investigated.

Assuming that $\alpha$ and $\chi$ for a molecule in its ground vibrational state have nearly the same values for the molecule in an excited vibrational level, the results of the calculation of $I(\lambda)$ for the rotation band can be used to compute the absorption coefficient for vibration-rotation bands as well. The strength of a line in a vibration-rotation band of an asymmetric rotor is given by

$$\frac{S_{J' n'}}{S_{J n}} = \frac{8 \pi^3}{3 \hbar c} \nu_T \left(1 - e^{-\sigma \nu_T} \right) \frac{N_i T e^{-\beta E_J n}}{Q(n)} \left| \mu_{in} \right|^2 \sum_{J' m'} \left| \phi_{J'n'} \right|^2$$

(12)

where $\nu_T = \frac{\nu_{J'n'}}{J' \tau n}$ is the transition frequency. $J$ and $\tau$ label
Figs. 7, 8, and 9. The calculated mean absorption coefficients at 250° K, 300° K, and 500° K. The dashed lines refer to the classical calculations. The solid lines refer to the modified quantum mechanical calculations.
$K_\nu$ 250°K
(modified)

$K_\nu$ atm$^{-1}$ cm$^{-1}$

$\nu$ cm$^{-1}$
the rotational states of the molecule and \( n \) represents the vibrational quantum numbers. \( N_0 \) is again the density of absorbing molecules at the temperature \( T_0 \) and one atmosphere, \( E_{J \tau n} \) is the energy of the lower state, \( Q(T) \) is the total partition function, \( M_{i' n'} \) is the vibrational dipole transition matrix element and \( \phi_{J' \tau' M'} \) are the rotational direction cosines. The total integrated strength for the vibrational transition is

\[
\alpha_{n'}^{n} = \sum_{J' \tau' n} S_{J' \tau' n} \tag{13}
\]

Assuming that the Hamiltonian is separable in the sense that

\[
E_{J \tau n} = E_n + E_{\tau J}
\]

and \( Q(T) = Q_v(T) \cdot Q_R(T) \) where \( Q_v \) is the vibrational partition function and \( Q_R \) is the rotational partition function, equation (13) may be written as

\[
\alpha_{n'}^{n} = \frac{8\pi^3 N_0 T_0}{3\hbar c} \frac{e^{-\frac{\theta E_n}{T}}}{Q_v(T)} \left| M_{n'}^{n} \right|^2 \left\{ \nu \left( 1 - e^{-\theta \nu} \right) \right\} \sum_{J' \tau' n'} \left| \phi_{J' \tau' n'} \right|^2 \tag{14}
\]

where

\[
\left\{ \nu \left( 1 - e^{-\theta \nu} \right) \right\} = \sum_{J \tau J' \nu} \nu \left( 1 - e^{-\theta \nu} \right) \frac{e^{-\frac{\theta E_J}{T}}}{Q_R(T)} \sum_{M M'} \left| \phi_{J' \tau' M'} \right|^2
\]

\[
= \nu_n^{n'} \left( 1 - e^{-\theta \nu_n^{n'}} \right).
\]
\( \nu_n' \) is the band center for the \( n \rightarrow n' \) transition. In turn the total band strength of a spectral region may be estimated using a "pseudo harmonic" oscillator model of the vibrational levels. The expression for the total strength is

\[
\alpha(T) = \sum_{n_i=0}^{\infty} \alpha_{n_i} + \delta_i 
\]

\[
= \frac{8\pi^3}{3hc} \frac{N_{0}T_{0}}{I} \left( \prod_{i=1}^{l} |\nu_{0i}^{2}| \right) \nu_{0} \left( 1 - e^{-\delta \nu_0} \right) \prod_{i=1}^{l} \frac{1}{(1 - e^{-\delta \nu_i})}\delta_i 
\]

(15)

where \( l \) is the number of degrees of freedom for the molecule; \( \nu_{0} \) is the band center of the spectral region and \( \nu_{i} \) is the vibration frequency of the \( i^{th} \) state. From equation (15) substituting \( \frac{N_{0}T_{0}}{I} \prod_{i=1}^{l} |\nu_{0i}^{2}| \)

for \( \frac{N_{0}T_{0}}{I} \nu_{B}^{2} \) in equation (10) and (1) gives the equation

\[
k_{\nu}(T) = \frac{\alpha(T)\nu(1 - e^{-\delta \nu})}{\nu_{0} \left( 1 - e^{-\delta \nu_{0}} \right)} \frac{I}{Q_{R}} \frac{1}{\theta(A-B)^{2}} \]

(16)

for the absorption coefficient in the region of vibration bands. Here \( \lambda - \lambda_{0} \) is given by

\[
\lambda - \lambda_{0} = \frac{\nu_{0} - \nu}{2} \left( \frac{\theta}{A-B} \right)^{\nu_{2}} 
\]

(17)

\( \alpha(T) \) may be calculated from a measurement of the strength at \( T_{0} \).
It has been demonstrated that the mean absorption coefficient of an asymmetric top molecule may be calculated from classical mechanics. An expression for the absorption coefficient was given in terms of the power spectrum—the Fourier transform of the molecular dipole autocorrelation function. This was described by Gordon. The mean absorption coefficient was obtained when a classical model for the rotation of a molecule was used to evaluate the autocorrelation function. The expressions for the mean absorption coefficient have been parameterized so that the temperature dependence of the coefficient may be easily determined. Furthermore, this model of the absorption due to an asymmetric rotor was based entirely on the dynamics of an asymmetric rotor. A comparison of the results of the classical calculations to those of quantum mechanical calculations revealed that the classical value of the absorption coefficient was less than the quantum mechanical value. It was suggested that the agreement between the classical and quantum mechanical calculations may be improved by introducing a correction.

\[
\frac{\alpha(T)}{\alpha(T_0)} = \frac{I_g}{I_0} \left( \frac{1 - e^{-\hbar c \nu_0 / kT}}{1 - e^{-\hbar c \nu_0 / kT_0}} \right) \prod_{i=1}^{L} \left(1 - e^{-\hbar c \nu_i / kT} \right) e^i
\]  

(18)
for the integers which appear in the quantum mechanical transition matrix elements into the classical calculations. Finally, assuming the parameters $\alpha$ and $\beta$ for a vibration-rotation band are nearly equal to the parameters for the pure rotation spectrum, the results for the power spectrum of the rotation band may be applied to the calculation of the absorption coefficients in the vibration-rotation band.
THE MEAN ABSORPTION COEFFICIENT OF H$_2$O

In the following sections the mean absorption coefficient for water vapor will be used in calculations of the infrared radiative flux coming from pure water vapor atmospheres. Several vibration-rotation absorption bands as well as the pure rotation band contribute to the infrared absorption due to water vapor. In Table 2 the parameters needed to calculate the absorption coefficients are listed. The values of the parameters were given by Penner and Varanasi. They were compiled from measurements of the band strengths at high temperatures and high pressures performed by Goldstein. The strengths of the $\nu_1$ and $\nu_3$ bands in the 2.7 $\mu$m region were approximated from the data given by Penner and Varanasi and an estimate of the ratio of the $\nu_1$ to $\nu_3$ band strengths given by Gates et al. The band type refers to the principal moment of inertia of the molecule along which the instantaneous dipole moment is aligned for the vibrational transition. Gates et al give the band types in the 2.7 $\mu$m region, and Benedict and Calfee give the types for the 6.3 $\mu$m and 1.87 $\mu$m bands. The power spectrum described in the preceding section was obtained for a B type band. Strictly speaking, applying these results to the A type bands will lead to errors.
Table 2.

List of vibration-rotation bands contributing to the infrared absorption spectrum of water vapor. $\alpha(300^\circ K)$ is the integrated band strength for the given spectral region.

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<thead>
<tr>
<th>Spectral Region ($\mu\lambda$)</th>
<th>Band Center (cm$^{-1}$)</th>
<th>Transition</th>
<th>$\alpha(300^\circ K)$ (atm$^{-1}$cm$^{-2}$)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>1595</td>
<td>000-010</td>
<td>225</td>
<td>B</td>
</tr>
<tr>
<td>2.7</td>
<td>3151</td>
<td>000-020</td>
<td>3.2</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>3652</td>
<td>000-100</td>
<td>17</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>3756</td>
<td>000-001</td>
<td>174</td>
<td>A</td>
</tr>
<tr>
<td>1.87</td>
<td>5332</td>
<td>000-011</td>
<td>21.6</td>
<td>A</td>
</tr>
<tr>
<td>1.38</td>
<td>6874</td>
<td>000-021</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7252</td>
<td>000-101</td>
<td>15.6</td>
<td></td>
</tr>
</tbody>
</table>
Nevertheless, it is expected that these errors are no larger than the ones already inherited from the classical calculation of the autocorrelation function used to obtain the power spectrum.

The calculation of the absorption coefficient for the pure rotation band was described in the last section. The contributions to the coefficient from the vibration-rotation bands were computed from equations (16), (17), and (18). In the event that two or more bands overlapped the resulting absorption coefficient was the sum of the contributions from each band.

This model for the absorption coefficient has a number of limitations which prohibit its application to general atmospheric problems. First of all the concept of a mean absorption coefficient is valid only in the limit of high pressures where the effect of the shape of the lines on the absorption is no longer significant. At lower pressures this model severely overestimates the actual absorption. Secondly, the power spectrum was calculated for values of $\lambda$ less than $\lambda_{\text{max}} = 6.50$. Even though the maximum value of the power spectrum is several orders of magnitude larger than its value at $\lambda_{\text{max}}$, the absorption at the wavenumbers corresponding to the value of $\lambda_{\text{max}}$ is still large for large optical path lengths. Thus the effect of very weak
lines in the wings of the infrared bands on the atmospheric absorption is neglected by this model. Nevertheless, the model offers two important improvements over a gray model of absorption. First, it allows for windows between the absorption bands, and secondly, it offers a simple method for incorporating the temperature dependence of the absorption coefficient into radiative transfer calculations.
RADIATIVE TRANSFER IN A DENSE WATER VAPOR ATMOSPHERE

If the oceans were evaporated the resulting atmosphere would be a very heavy water vapor atmosphere as described by Munk. Assuming that the absorption coefficient of the water vapor atmosphere were gray, Munk deduced that a high surface temperature—1700° K—would be maintained with only a moderate flux of thermal radiation coming from the surface of the earth—1.15 x 10^4 ergs cm^{-2} sec^{-1}. Munk suggested that such a high surface temperature could not be maintained if the nongrayness of the atmosphere were accounted for.

An improved calculation of the radiative flux in this heavy water vapor atmosphere was performed using the calculation of the mean absorption coefficient of H_2O to describe the water vapor absorption spectrum. Since this model of the absorption allows for the existence of windows between the absorption bands, it was expected that the radiative flux from the nongray atmosphere would be significantly larger than the flux from a gray atmosphere with the same temperature profile.

An expression for the total radiative flux in the atmosphere is readily obtained from the equation of radiative transfer. Since the height of the atmosphere is small
in comparison to the radius of the earth, the atmosphere is assumed to have planar symmetry. Due to the large densities encountered in the heavy water vapor atmosphere, it is assumed that the atmosphere is in local thermal equilibrium (LTE).\textsuperscript{20} The equation of radiative transfer for a planar atmosphere in LTE is\textsuperscript{21}

\[ -\mu \frac{dI_\nu}{dz} = k_\nu(T(z))P(z)(I_\nu(z,\mu) - B_\nu(T(z))) \] \hspace{1cm} (19)

\( \mu \) is the cosine between the normal to the planetary surface and the direction of the outgoing ray of radiation. \( Z \) is the altitude measured from the surface. \( k_\nu \) is the absorption coefficient (in atm\(^{-1}\) cm\(^{-1}\)). In this case the mean absorption coefficient was used. \( P \) is the pressure and \( T \) is the temperature. \( I_\nu \) is the intensity of radiation at the wavenumber \( \nu \) in the direction of \( \mu \) at the altitude \( Z \) per unit solid angle per unit wavenumber interval. Finally \( B_\nu \) is the equilibrium intensity at the wavenumber \( \nu \) as given by the Plank distribution function at the temperature \( T \). The optical depth is traditionally defined as

\[ d\tau_\nu = -k_\nu(T(z))P(z)dz \] \hspace{1cm} (20)

with the condition that \( \tau_\nu = 0 \) at the top of the atmosphere. For this change of variables the equation of transfer becomes

\[ \mu \frac{dI_\nu}{d\tau_\nu} = I_\nu - B_\nu \] \hspace{1cm} (21)
The boundary conditions used in the integration of the transfer equation were as follows: At the bottom of the atmosphere the earth radiates like a black body at a temperature $T_G$ -- the surface temperature.

$$I_v\left(\tau_{m_v}, \mu\right) = B_v\left(T_G\right) \quad \text{for } \mu > 0$$  \hspace{1cm} (22)

$\tau_{m_v}$ is the maximum depth at the wavenumber $v$, and it corresponds to $Z = 0$. At the top of the atmosphere there is no source of incoming radiation

$$I_v\left(0, \mu\right) = 0 \quad \text{for } \mu < 0$$  \hspace{1cm} (23)

Equation (21) is readily integrated with the boundary conditions (22) and (23) to give

$$I_v\left(\tau_v, \mu\right) = B_v\left(T_G\right) e^{\left(\frac{\tau_v}{\mu} - \tau_{m_v}\right)} \quad \text{for } \mu > 0,$$

$$+ \int_{\tau_v}^{\tau_{m_v}} B_v\left(\tau'\right) e^{\left(\frac{\tau_v - \tau'}{\mu}\right)} \frac{d\tau'}{\mu} \quad \text{for } \mu > 0,$$

and

$$I_v\left(\tau_v, \mu\right) = -\int_{0}^{\tau_v} B_v\left(\tau'\right) e^{\left(\frac{\tau_v - \tau'}{\mu}\right)} \frac{d\tau'}{\mu} \quad \text{for } \mu < 0.$$  \hspace{1cm} (25)

The dependence of $B_v$ on $\tau_v$ is given through the temperature $T(\tau_v(z))$. The radiative flux is given by multiplying $I_v$ by $\mu$ and integrating over the total solid angle.
\[ \pi F_\nu (\tau_\nu (z)) = \int d \Omega (\mu, \phi) \mu I_\nu (\tau_\nu (z), \mu). \] (26)

Multiplying equations (24) and (25) by \( \mu \) and integrating over the total solid angle gives
\[ \pi F_\nu (\tau_\nu) = 2\pi B_\nu (T_\nu) E_n (\tau_{m_\nu} - \tau_\nu) \]
\[ + 2\pi \int_{\tau_\nu}^{\tau_{m_\nu}} B_\nu (\tau') E_2 (\tau - \tau') d\tau' - 2\pi \int_0^{\tau_\nu} B_\nu (\tau') E_2 (\tau_\nu - \tau') d\tau'. \] (27)

\( E_n (T) \) are exponential integral functions of order \( n \). In the event that there are no sources of local heating within a planar atmosphere conservation of energy constrains the total flux
\[ \pi F = \pi \int_0^{\infty} F_\nu (z) d\nu \] (28)to a constant value.\(^2\)

The total radiative fluxes were computed at several altitudes in a water vapor atmosphere similar to the one for which Munk did the gray calculations. The atmosphere was assumed to be in a state of hydrostatic equilibrium.
\[ dp = - \rho g dz \] (29)
\( \rho \) is the density of the water vapor and \( g \) is the gravitational acceleration—\( -980 \) cm sec\(^{-2}\). It was assumed that the water vapor behaved as an ideal gas.
\[ P = \rho RT \] (30)
where \( R \) is the gas constant for water vapor (in ergs gm\(^{-1}\))
degree$^{-1}$). Combining equations (29) and (30) gives

$$\frac{dP}{P} = - \frac{qdz}{RT(z)}.$$  \hfill (31)

Equation (31) implies that once the temperature profile of the atmosphere is known all of the other thermodynamic properties can be determined. Furthermore, the temperature and pressure profiles can be used to calculate the optical depths from the absorption coefficients. These in turn lead to the evaluation of the flux from equations (27) and (28).

Ideally it is possible to solve the equation of transfer by discovering the temperature profile which results in a constant value of the total flux at all altitudes. However, it is not possible to apply the present model of absorption to this end. Due to the large optical paths encountered in this heavy water vapor atmosphere the absorption due to weak lines in the far wings of the absorption bands is not negligible. Thus the constancy of the net flux can only be approximated.

Munk used a method developed by Ostriker$^{22}$ to calculate the temperature profile of a gray atmosphere with a source of thermal radiation at its bottom. Ostriker found that for a thick finite gray atmosphere the temperature profile was nearly the same as that given by the Eddington approximation.
\[ T(\tau) = T_e \left[ \frac{3}{4} \left( \tau + \frac{3}{2} \right) \right]^{1/4} \]  

(32)

\( \tau \) is the frequency independent optical depth. The constant radiative flux \( \pi F \) is related to an equivalent temperature \( T_e \) by

\[ \pi F = \sigma T_e^4 \]  

(33)

where \( \sigma \) is the Stefan-Boltzmann constant---5.67 \( \times \) 10\(^{-5} \) ergs sec\(^{-1} \) cm\(^{-2} \) degree\(^{-4} \). For \( \tau = 0 \), the temperature at the top of the atmosphere is

\[ T_o = \left( \frac{1}{2} \right)^{1/4} T_e \]  

(34)

The temperature gradient within the atmosphere is given by

\[ \frac{dT}{dZ} = \frac{1}{4} \frac{g}{R} \left( 1 - \left( \frac{T_o}{T} \right)^4 \right) \]  

(35)

It is seen that as \( T \) approaches \( T_o \) the temperature gradient for the region of small optical depth is zero. Furthermore, for regions of large optical depths where \( T \gg T_o \) the temperature gradient assumes a constant value \( g/4R \) independent of the magnitude of the gray absorption coefficient.

This constant value is equivalent to the adiabatic lapse rate for an atmosphere of polyatomic gases such as water vapor.\(^{23} \) The results of Munk's calculations are given in Table 3 for a water vapor atmosphere with a surface pressure of 269 atmospheres and a given total flux of \( 1.15 \times 10^4 \) ergs cm\(^{-2} \) sec\(^{-1} \).
Table 3.

The results of Munk's calculations for a thick water vapor atmosphere. \( \pi F \) was calculated from tidal dissipation in a boundary layer at the surface of the earth. \( \tau \) was calculated from an assumed value of the Rossland mean coefficient for the earth.\(^1\)

| \( T_0 \) | 100° K |
| \( T_e \) | 119° K |
| \( T(\tau = 1) \) | 126° K |
| \( T_g(\tau = \tau_m) \) | 1700° K |
| \( \pi F \) | \( 1.15 \times 10^4 \) ergs cm\(^{-2}\) sec\(^{-1}\) |
| \( \tau \) | \( 5.75 \times 10^4 \) |

The following temperature profile which closely approximates the profile in the gray calculations was used for the nongray calculations of the total flux. The temperature lapse rate was assumed to be at the adiabatic value from 1700° to 126° K. For the gray optical depth \( \tau \geq 1 \) which corresponds to this temperature region the gradient deviates from the adiabatic value by less than three percent. From the 126° K level the temperature decreased to 100° K along a constant gradient equal to half the adiabatic gradient.
Finally, there was an isothermal layer at the top of the atmosphere. The top of the atmosphere was arbitrarily set at 10^{-4} \text{ atm}. The absorption by vapor above this level had a negligible effect on the total flux.

The total radiative flux at the planetary surface and at the top of the regions designated by the constant lapse rates were numerically calculated from equations (27) and (28). Each region of constant lapse rate was subdivided so that a Gaussian quadrature method could be used to integrate equation (20) to obtain the optical depth within each sub-region. The integration in equation (27) over optical depth was performed using Simpson's rule. Finally, a trapezoid technique was used to approximate the integration of the resulting fluxes over all wavenumbers. The temperature profile and the resulting fluxes calculated from equations (27) and (28) are given in Table 4.

Contributions to the total flux from the relatively transparent region beyond 8000 \text{ cm}^{-1} were not included in these calculations. Although less than 10\% of the total flux of a black body at 1700^\circ \text{ K} is at wavenumbers greater than 8000 \text{ cm}^{-1}, the value of the flux for this spectral region from a 1700^\circ \text{ K} black body (4.3 \times 10^7 \text{ ergs sec}^{-1} \text{ cm}^{-2}) is large enough to completely swamp the value of the flux in the region of the vibration-rotation bands. Including the contributions of this region to the total flux would have hidden some of
the important differences found between the results for the gray and the nongray calculations.

Table 4.

Radiative fluxes calculated for a heavy nongray atmosphere. The temperature profile is close to that found in the gray atmosphere.

<table>
<thead>
<tr>
<th>Altitude (KM)</th>
<th>Pressure (atm)</th>
<th>Temperature (°K)</th>
<th>Flux (ergs sec^{-1} cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>318.4</td>
<td>1.00 x 10^{-4}</td>
<td>100.0</td>
<td>2.28 x 10^{5}</td>
</tr>
<tr>
<td>306.4</td>
<td>1.28 x 10^{-3}</td>
<td>100.0</td>
<td>2.23 x 10^{5}</td>
</tr>
<tr>
<td>296.6</td>
<td>8.12 x 10^{-3}</td>
<td>126.0</td>
<td>2.22 x 10^{5}</td>
</tr>
<tr>
<td>241.2</td>
<td>1.00</td>
<td>420.0</td>
<td>1.04 x 10^{4}</td>
</tr>
<tr>
<td>0</td>
<td>269</td>
<td>1700</td>
<td>14.9</td>
</tr>
</tbody>
</table>

It was observed that for the levels at 126°K and above the radiative flux was relatively constant. The increase in the total flux is due primarily to the strong absorption in the pure rotation band. It must be remembered that the absorption due to weak lines in the wings of the
bands is neglected by the present model. Nevertheless, it is expected that the value of the flux given for the spectral region below 8000 cm$^{-1}$ is representative of the value that would be obtained by more careful considerations. Neglecting the absorption in the far wings of the absorption bands is partly compensated for by the fact that the model accounts for the temperature dependence of the widths of the band. As the temperature increases, the widths of the bands increase; thus the absorption in the wings of a band becomes evident at only a slightly higher temperature than it would if the weak lines are considered. Since the radiation emitted by an atmosphere comes predominantly from atmospheric regions of small optical depths, the emitted flux in the wing of a band comes from a region of only a slightly higher temperature than it would if the weak lines are included in the calculations.

Due to the low pressures for the 126° K level and above, the resulting flux calculations are expected to represent a lower limit of the total flux. The present model does not allow for individual absorption lines. Consequently, a considerable amount of radiative flux which would normally pass freely between these lines is neglected.

Finally, the accuracy of the numerical calculations aside from the limitations imposed by the model of the
absorption coefficient is estimated at 5%.

There are some interesting differences between the gray and nongray calculations of the total flux. First, as expected, the total flux calculated using the mean absorption coefficient is nearly twenty times that of the gray calculation. This is due to the substantial amount of energy passing through the atmosphere in the spectral regions between the absorption bands. Furthermore, this result implies that a 1700° K surface temperature would not be maintained by an energy source with a flux of only $1.15 \times 10^4$ erg sec$^{-1}$ cm$^{-2}$. Secondly, whereas the total radiative flux in the gray calculation is postulated to be constant, it was found for the nongray calculations that the radiative fluxes in the lower regions of the atmosphere were far less than the values at the top of the atmosphere. The lower regions of the nongray atmosphere were found to be convectively unstable. For these regions the difference between the total flux and the radiative flux is presumably equivalent to the convective energy flux. Since the atmosphere is very dense at the lower altitudes and since the convective energy fluxes are relatively small the resulting temperature gradient for the convective regions are expected to be close to the value of the adiabatic rate. Finally, it is noted that water would ordinarily be in a solid phase at 126° K and $8.12 \times 10^{-3}$ atm. The resulting optical properties
of the upper region would have to be altered if this condition were incorporated into the solution. On the other hand, demanding that the water be in a vapor state at all levels in the atmosphere would require a temperature at this pressure of at least 277.5° K. Following an adiabat from this level down to the surface would result in a surface temperature of 4000° K. Surely other physical processes such as the melting of the earth and the photodissociation of water vapor would have occurred long before this temperature would have been reached.

In summary, a comparison was made between Munk's gray calculations of radiative transfer in the atmosphere which would have been formed if the oceans had been evaporated and similar nongray calculations using the mean absorption coefficient for H₂O. Although this model of the absorption coefficient did not include the weak lines in the far wings of the bands, it is expected that since the model did account for the temperature dependence of the wings, the value of the radiative flux emitted by the atmosphere was representative of that which would have been obtained using methods which included the absorption due to the weak lines. The mean absorption coefficient is applicable only for gases at high pressure. Owing to the low pressure region at the top of the atmosphere, it was expected that
the value of the flux obtained was a lower limit. When
the temperature profile of the gray atmosphere was used for
the nongray calculations, it was found that the radiative
flux in the upper regions of the nongray atmosphere was
relatively constant. In contrast to the condition of con-
stant flux postulated in the gray calculations, the fluxes
for the nongray atmosphere in regions of large optical
depths were considerably smaller than the value of the flux
at the top of the atmosphere. For these regions energy was
presumably transported by convection. Finally, it was
observed that even in the event that the large radiative
flux at wavenumbers greater than 8000 cm\(^{-1}\) was neglected,
the nongray calculation predicted a total flux some
twenty times the value given by the gray calculations.
This implied that the dissipation of energy in the boundary
layer calculated by Munk would not be large enough to
maintain the given surface temperature.
THERMAL RADIATIVE FLUX FOR
PURE WATER VAPOR ATMOSPHERES

If the amount of radiation incident on the atmosphere of a planet having bodies of water on its surface is sufficiently large, a "runaway greenhouse" effect will occur. The absorption of thermal radiation due to the water vapor in the atmosphere results in a high surface temperature which in turn leads to the evaporation of more water thus increasing the absorption of the atmosphere. Several calculations which attempt to ascertain the necessary conditions for the runaway effect have been recently presented. Ingersoll\textsuperscript{24} and Rasool and De Berg\textsuperscript{25} have performed gray calculations, and Pollack\textsuperscript{2} has performed non-gray calculations to determine whether or not Venus lies within the runaway regime. Among the models Pollack considered for the atmosphere of Venus were pure water vapor atmospheres having a constant value of the relative humidity in their tropospheres. Although such atmospheres are unlikely, the models offer results which may be used to estimate the limits within which a runaway greenhouse effect occurs.

In this section the flux of thermal radiation emitted from a pure water vapor atmosphere was calculated for
several values of the surface temperature assuming a constant relative humidity in the troposphere. The pressure at a given temperature level in a pure water vapor atmosphere is given by the product of the relative humidity and the equilibrium vapor pressure of water vapor at that temperature. Thus, specifying the relative humidity and the surface temperature of a pure water vapor atmosphere determines the temperature and pressure profiles which in turn may be used to calculate the total radiative flux emitted at the top of the atmosphere as described in the previous section. In calculating the flux for an atmosphere of constant relative humidity the atmosphere was divided into several regions of constant lapse rates. The resulting profiles were reasonable representations of the temperature profiles demanded by the condition of constant relative humidity. The temperature at the top of the atmospheres was $215^\circ$K. This temperature was chosen for the purpose of making a comparison between these results and those of the similar calculations done by Pollack.$^2$ The total fluxes for atmospheres with 25% and 100% relative humidities are presented in Table 5.

The values of the fluxes obtained using the calculation of the mean absorption coefficient are expected to be low owing to the over estimation of the absorption by this
model at the low pressures encountered in these atmospheres. For comparison, Pollack\(^2\) has calculated that the flux of thermal radiation coming from a pure water vapor atmosphere with a 300\(^\circ\)K surface temperature, a 50% cloud cover, and a relative humidity profile similar to that found on the earth, should be 0.43 cal cm\(^{-2}\) min\(^{-1}\). The humidity profile used in the calculation was greater than 25% at all levels. The tropopause was set at 215\(^\circ\)K. The cloud temperature was thirty degrees cooler than the surface temperature. The clouds were assumed to be infinitely opaque which means that they effectively become the source of radiation at the lower boundary of the atmosphere in the case of 100% cloud cover. The model of water vapor absorption used by Pollack was based on experimental measurements of the average transmission of water vapor in the infrared.\(^{26,27}\) Since it allows for the pressure broadening of the absorption lines, it is expected that Pollack's model is appropriate to the calculations of radiative transfer in planetary atmospheres where low pressures and long path lengths prevail.

The value of the flux of thermal radiation coming from an atmosphere with a 25% relative humidity and 50% cloud cover where the cloud temperature is thirty degrees cooler than the surface is obtained by averaging the fluxes
for the cases of 270°K and 300°K surface temperatures. This gives for the outgoing flux 0.346 cal cm\(^{-2}\) min\(^{-1}\) which is roughly 80\% of the value calculated by Pollack. Since the relative humidity in the model used by Pollack was higher than 25\%, the results given in Table 5 for 100\% humidity suggest that the value of the flux obtained for the atmosphere with the constant 25\% humidity should have been larger than that given by Pollack. It is seen that for regions of small pressures the mean absorption coefficient can lead to substantial errors in the evaluation of the outgoing flux.

Knowledge of the planetary albedo in conjunction with the information given in Table 5 allows certain conclusions to be drawn concerning the amount of incident solar flux necessary to maintain a given surface temperature. For example if a planet with a pure water vapor atmosphere had an albedo \(A\) equivalent to the earth's albedo \(0.40\)\(^{20}\) and the incident radiative flux \(F_s\) on this atmosphere were the same as the present solar radiation incident on the earth's atmosphere \(2.00\) cal cm\(^{-2}\) min\(^{-1}\), providing the planet were rapidly rotating (as does the earth), the resulting flux of thermal radiation \(0.30\) cal cm\(^{-2}\) min\(^{-1}\).
would maintain only a moderate surface temperature.

Table 5.
Flux of thermal radiation as a function of surface temperature. RH is relative humidity.

<table>
<thead>
<tr>
<th>Surface Temperature (°K)</th>
<th>Flux (cal cm⁻² min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25% RH</td>
</tr>
<tr>
<td>270</td>
<td>.313</td>
</tr>
<tr>
<td>300</td>
<td>.378</td>
</tr>
<tr>
<td>343</td>
<td>.455</td>
</tr>
<tr>
<td>373</td>
<td>.500</td>
</tr>
</tbody>
</table>
SUMMARY

A mean absorption coefficient for water vapor which is applicable to conditions of high pressure was computed using a method which is based on the classical description of the rotation of the molecule. When the results for the calculation of the absorption coefficient in the pure rotation spectrum of H₂O are compared with those from quantum mechanical calculations, the classical results were significantly lower. It was suggested that a correction could be made to the classical calculations to improve their agreement with the quantum mechanical calculations. The model of absorption had two important features: 1) It allowed for the existence of windows between the absorption bands. 2) It offered a convenient method for incorporating the temperature dependence of the absorption coefficient into radiative transfer calculations.

The values obtained for the mean absorption coefficient were applied to a calculation of the radiative flux in a heavy water vapor atmosphere having the same temperature profile as the atmosphere used by Munk in his gray approximation. A comparison was made between the gray and the nongray results. Since both atmospheres were planar, and since the only source of energy was located at the
earth's surface in both cases, conservation of energy demanded that the total flux be constant—indeed independent of the altitude. Due to the approximate nature of the mean absorption coefficient, this condition was only approximately satisfied in the nongray atmosphere. Two important differences were discovered between the gray and nongray results. First, the total flux emitted by the nongray atmosphere was many times that emitted by the gray atmosphere. This implied that the high surface temperatures obtained by Munk could not be maintained by a nongray atmosphere. Secondly, unlike the gray atmosphere part of the energy in the lower regions of the nongray atmosphere was transported by convection.

Finally, it was found that the value of the flux of thermal radiation emitted by a low pressure water vapor atmosphere using the mean absorption coefficient appeared to be less than that calculated using a model of absorption which accounts for the pressure broadening of the absorption lines. The lower value was probably due to the fact that the mean absorption coefficient seriously overestimates the absorption of water vapor at low pressures. The values of the thermal radiative flux were given for pure water vapor atmospheres having constant relative humidities in their tropospheres. The calculations were done for several
values of the planetary surface temperature. Such data may be used to estimate the flux of incident radiation needed to maintain a given surface temperature.
ACKNOWLEDGEMENTS

I happily acknowledge my indebtedness to a large number of people who have helped me in this project. I owe special thanks to Dr. William H. Miller who introduced me to the technique used to calculate the mean absorption coefficient; to Professor William D. Gwinn for providing me with a computer code which did the line strength and position calculations for the rigid asymmetric rotor; and to Professor Kenneth M. Watson for his advice which lead me to the solutions of the most difficult problems encountered in this work. Finally my wife, Stella, should be credited for producing a beautifully typed manuscript. This work was supported by the U. S. Atomic Energy Commission.
REFERENCES


4. G. D. T. Tejwani and P. Varanasi, *JQSRT* 10, 373 (1970). The expression given in this reference for the number of molecules per unit volume in the initial state of a transition is incorrect and the subsequent results for the line strengths are in error. Dr. Tejwani informs me that the error is about 15% at 1200°K, and that owing to the approximate nature of the calculations he does not intend to modify the results at present.


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