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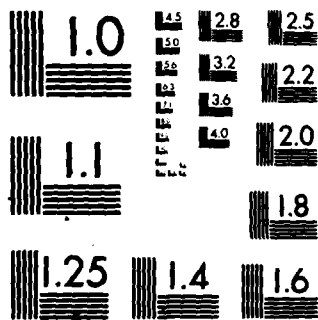
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6 ATMOSPHERIC ABSORPTION OF RADIATION BY WATER.

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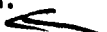
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water continuum have been identified. One of these mechanisms- pressure induced absorption- has been shown to play an important role in the interpretation of laboratory spectra which are currently used as the basis for empirically modeling the water continuum. 

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INTRODUCTION

The absorption of microwave and infrared radiation by H_2O molecules in the Earth's atmosphere is a problem of considerable importance from both a theoretical¹ and a practical standpoint². In atmospheric windows (e.g. regions centered around 1000 cm^{-1} , 2500 cm^{-1} , etc.) where there are no strong absorption bands located, there is, however, considerable residual absorption. This is referred to as "continuum absorption" because of the absence of any detailed structure.

Although a large number of experimental studies have been carried out, there is at present no consensus as to the origin of this absorption. Many different mechanisms have been proposed: far wings of allowed lines³, water dimers⁴, pressure induced absorption⁵, charge stabilized molecular complexes⁶, etc. While there is some disagreement regarding the mechanism responsible for this absorption, there is complete agreement on the most salient experimental result: the absorption varies quadratically with the density of water molecules^{7,8}. This implies that the absorption is due to a "binary effect"; i.e. a mechanism involving two H_2O molecules. This fact would appear to rule out absorption involving complexes containing more than two molecules, and far wing absorption of dimer lines, since these processes would depend on higher powers of the water density.

A second important experimental feature, the temperature dependence of the absorption, is less conclusively known. Conflicting reports have been published^{9,10} as to whether the continuum increases or decreases as the temperature is increased. The most comprehensive set of measurements (those of Burch and collaborators^{9,11}) seem to indicate a strong negative temperature dependence. That is, the absorption decreases markedly as the temperature increases. This has been interpreted by some workers as unassailable evidence for the water dimer mechanism¹². This conclusion is premature, however, until one knows with some assurance the temperature dependence of the other mechanisms. At present, the temperature dependence of the absorption by the far wings of allowed lines is not known, although preliminary work on this problem has been carried out at AFGL. Detailed calculations are now possible because of the formulation of a correct quantum mechanical theory¹³ which is valid over the entire profile of an allowed spectral line (see Appendix A). This work will be discussed in the following section, along with some other conclusions from the present research. Because of the complexity of the problem, much additional work will be necessary before the results can be applied to the atmospheric absorption.

We note in passing that because of the nature of the water-water potential, the allowed spectrum will have contributions from bound-bound transitions (dimers), bound-free transitions, and free-free transitions (usual pressure broadening).

2. There are three types of operators which will have an N^2 dependence; this implies that the integrated intensities associated with these operators will be quadratic in the water density. These are:

(A). Cross correlation function of the form

$$\langle \vec{\mu}_1^A \cdot \vec{\mu}_2^A \rangle \quad (4)$$

where the subscripts refer to the dipole operator associated with two different molecules. This operator has heretofore been neglected, since in the absence of anisotropic interactions, the associated wave functions can be written as a product and this term would then vanish. However, one effect of the large dipole-dipole interaction will be to mix the rotational states during collisions implying that the rotational quantum numbers will no longer be strictly valid. In this case, one may get absorption through this operator which may account for part of the continuum absorption. Further research in this direction is being pursued.

(B). Interference terms between the allowed and induced dipoles of the form

$$\langle \vec{\mu}_1^A \cdot \vec{\mu}_{12}^I + \vec{\mu}_{12}^I \cdot \vec{\mu}_1^A \rangle \quad (5)$$

The theory for the absorption and lineshape for an operator of this type in the case of a simple diatomic gas (HD) has been published recently¹⁴. The significance of this operator vis-a-vis the water absorption in the atmosphere is not known at present. More experiments involving the measurement of the induced dipole in water will have to be carried out.

(C). Autocorrelation function of the induced dipoles of the form

$$\langle \vec{\mu}_{12}^I \cdot \vec{\mu}_{12}^I \rangle \quad (6)$$

THEORY

The absorption coefficient for a gas of N molecules can, quite generally, be written as the Fourier transform of the dipole moment correlation function¹³

$$\alpha(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega t} \langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle dt \quad (1)$$

where the wave functions implicit in the correlation function, and the Heisenberg dipole moment operators are N -body functions. Assuming that the dipole moment operator can be written in the form

$$\vec{\mu} = \sum_{i=1}^N \vec{\mu}_i^A + \sum_{\substack{j,k \\ =1}}^N \vec{\mu}^I(R_{jk}) \quad (2)$$

where $\vec{\mu}^A$ and $\vec{\mu}^I$ are the allowed and induced dipoles, respectively, one can decompose the absorption coefficient into individual N -body contributions as follows:

1. The only term proportional to N is the autocorrelation function of the allowed dipole moment operator

$$\langle \vec{\mu}_1^A \cdot \vec{\mu}_1^A \rangle \quad (3)$$

This leads to the usual allowed spectrum. The lineshape resulting from this operator including the effects of binary collisions has been derived and the resulting paper submitted to the Physical Revue for publication. (A copy of the paper is attached as Appendix A.) Detailed numerical computations for a realistic water potential are presently in progress at AFGL, although it will be some time before the results are completed. This theory, in contradistinction to previous theories, is applicable over the entire contour of the line. As expected, the absorption in the far wings is proportional to the square of the density in conformity with the experimental results. This theory also permits one to calculate the temperature dependence of the far wing absorption. From the detailed results computed with this theory, one will be able to answer the question as to whether the far wings of allowed lines can quantitatively explain the atmospheric absorption.

Recently, the theory for pressure induced absorption for asymmetric top molecules (e.g. H_2O) has been worked out¹⁵. The application of this theory will allow one to calculate the integrated absorption arising from this mechanism, and thus ascertain whether it plays a major role in the continuum atmospheric absorption.

Regardless of the outcome of the above question, it is clear as a result of the present investigation that pressure induced effects can play an important role in the interpretation of laboratory data. This data is currently being used to empirically model the continuum absorption, and for this to give realistic answers, one has to be sure exactly what one is measuring. For example, in an attempt to measure the effect of N_2 on the water continuum in the 4 micron region at 428K, Burch¹¹ found the ratio $C_{N,P}^0 / C_{S,W}^0$ (for the meaning of the symbols, see Ref. 11) to be approximately 0.12 which is much higher than the same ratio measured in other spectral regions. However, what he actually determined was the ratio $(C_{N,P}^0 + C_{N,W}^0) / C_{S,W}^0$, where $C_{N,W}^0$ is the contribution of the water induced nitrogen absorption which was neglected in the analysis. The magnitude of $C_{N,W}^0$ is much larger than $C_{N,P}^0$, so that what he determined was the ratio $C_{N,W}^0 / C_{S,W}^0$, and the experimental result is consistent with the theoretical estimate based on dipole-induced-dipole absorption¹⁶. A completely different set of mixing ratios of N_2 / H_2O would have to be used if one wanted to measure the effects of N_2 .

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RESULTS AND CONCLUSIONS

The research undertaken during the past year sponsored by AFOSR under their Mini-Grant program set out to answer three basic questions concerning the absorption of radiation by water in the Earth's atmosphere. These were:

1. Can one find a suitable lineshape, taking into account the breakdown of the usual impact approximations, to represent an isolated spectral line over its entire contour?
2. Assuming one has an adequate representation for the shape of an isolated line, can one then obtain reasonable agreement between theory and experiment for the water continuum by an incoherent superposition of lines corresponding to allowed transitions?
3. Are there any other mechanisms (in addition to the usual allowed dipole transitions in individual water molecules) which contribute significantly to the continuum absorption in the $0 - 1200 \text{ cm}^{-1}$ region of the spectrum? More specifically, what role, if any, do collision induced effects play?

The answer to question 1 is obviously "yes". Such a theory has been formulated and is attached as Appendix A.

The final answer to question 2 must await a complete numerical analysis based on this theory. Some progress has been made primarily by Dr. S. A. Clough at the Air Force Geophysics Lab, in collaboration with Dr. R. W. Davies. Recently we have obtained the necessary computer programs to carry out this analysis. Preliminary calculations have been very encouraging¹⁷.

The answer to question 3 as discussed in the previous section is that there are other mechanisms which bear further research. With the recently developed theory for collision induced absorption in asymmetric top molecules, one can calculate this effect and determine its significance for the continuum. In any event, it is clear that collision induced effects do play an important role in some of the laboratory studies which have been carried out, and must be considered when extracting experimental parameters which are to be used in modeling the continuum absorption.

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