

---

## Light Scattering Studies of the Atmosphere

H. A. Gebbie

*Phil. Trans. R. Soc. Lond. A* 1979 **293**, 413-417

doi: 10.1098/rsta.1979.0108

---

### Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

---

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

---

## Light scattering studies of the atmosphere

BY H. A. GEBBIE

*Department of Physics, Imperial College of Science and Technology, London, U.K.*

Despite a very detailed knowledge of the molecular composition of the atmosphere and of reliable forms of Mie theory to describe losses in condensed phases there are marked discrepancies between predicted losses and what is observed when infrared radiation passes through long atmospheric columns. There is a need to invoke the presence of new absorbing molecules which are almost certainly molecular complexes of water. The whole problem will be reviewed and recent evidence which points to a better understanding will be given. The range of wavelengths considered will be from 3  $\mu\text{m}$  to 3 mm.

### INTRODUCTION

When electromagnetic radiation has to be propagated through long columns of the atmosphere, spectral regions in which losses are small assume particular importance. The study of actual losses in the relatively transparent gaps between absorption lines in the infrared, millimetre wave and microwave spectral regions, has exposed deficiencies in our knowledge of the physics underlying the residual absorption phenomena. The problems certainly involve water, which is not only an important absorber by itself but, as a hydrogen bonding species, is likely to form molecular complexes which can also absorb. The energies which characterize the bonding of the complexes are such that in the range of temperatures found in the troposphere and stratosphere (say 220–320 K) significant changes in the concentration or possibly of the structure of the complexes can occur. This means that a variety of observable atmospheric phenomena is to be expected.

Traditionally the total atmospheric absorption at a given wavelength would be considered as predictable from the known particle contribution calculated by Mie theory and the known stable molecule contribution. The latter presumes that a complete list of the relevant transitions is available with appropriate linewidth parameters and that an adequate line shape model is used. When this is done, the stable molecule contribution can now be fairly well represented. However, there are still major discrepancies between prediction and observation in that there is frequently additional measured absorption in the gaps, which would have been expected to be most transparent. The term ‘anomalous absorption’ has been used to describe the additional component which, as yet, has no satisfactory explanation either in terms of molecules or particles.

Non-equilibrium molecular complexes of water appear to have been neglected in considering possible absorbers because, even if these are not thermodynamically stable, they will make a contribution to absorption if they have a finite lifetime. This contribution will be characterized by the eigenfrequencies’ intrinsic strengths and the lifetimes of the complexes. However, before the effects of any non-equilibrium species can be distinguished, it is important to recognize the existence of stable equilibrium dimers of water formed by hydrogen bonding. Their fundamental properties are now well established and predictions of their behaviour in various

[ 203 ]

conditions can be made. At one time it was thought that water dimers might be the sole cause of anomalous absorption in the millimetre and in the 10  $\mu\text{m}$  wavelength regions, but this is no longer a tenable hypothesis.

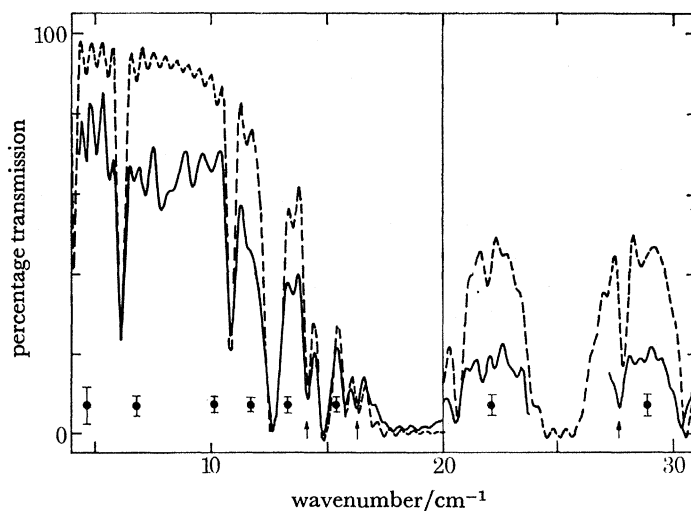


FIGURE 1. Comparison of observations (shown by the full line) with expectation (shown by the dotted line) of a transmission spectrum of the atmosphere measured above Mauna Kea in Hawaii (Moffat *et al.* 1977).

#### EVIDENCE FOR ANOMALOUS ABSORPTION IN THE REAL ATMOSPHERE

The clearest manifestation of anomalous absorption is in the millimetre wavelength region. For wavenumbers in the region of 10  $\text{cm}^{-1}$ , the loss in liquid or solid particles for most atmospheric conditions is negligible in comparison with molecular absorption. This is dominated by water and can confidently be predicted. The position, strength and width of the monomer pure-rotation water lines are known, and the dimer spectrum can be represented as a featureless contour which varies slowly with frequency. However, real atmosphere spectra (as in figure 1) show that, for a slant path through the whole atmosphere, transparency is less than expected, particularly between wavenumbers from about 7 to 10  $\text{cm}^{-1}$  where there is additional spectrally structured absorption. Similar results have been reported for measurements made over horizontal paths, and from such measurements it is found that anomalous absorption is particularly associated with high relative humidity and low temperatures. These spectra cannot at present be explained in terms of any known molecular species, though it should be mentioned that the features are very variable in both wavenumber and strength in most real atmosphere observations and this adds greatly to the difficulty of assignment. The most reproducible spectra have been found in conditions associated with a radiation fog when quite systematic behaviour with changing fog density has been observed. It is emphasized that even in these conditions the spectrum cannot be attributed to the liquid water particles of the fog themselves.

It should be noted that the strength of anomalous absorption is such that the phenomenon is only seen in the path lengths through a large part of the atmosphere or in horizontal paths of the order of 100 m. This, together with the technical difficulty of present measurement techniques in the 5–10  $\text{cm}^{-1}$  wavenumber region, probably accounts for the phenomena having been so little observed. It also points to the need for long path lengths when the phenomenon is studied in the laboratory.

## LABORATORY MEASUREMENT OF ANOMALOUS ABSORPTION

A useful property for distinguishing between various components of molecular absorption by water vapour in laboratory conditions is their behaviour with temperature. Monomer absorption will be expected to have a weak temperature dependence characterized in an exponential representation by an energy of the order of 0.05 eV per molecule. The dimer component will have a temperature dependence of absorption dominated by concentration changes which will have a characteristic energy of about 0.16 eV per molecule. Since this is the binding energy of the equilibrium dimer molecule, any different and, particularly, any steeper temperature dependence which is observed can be taken as indicative of the presence of some unidentified complex. Experiments to exploit this have been made at Appleton Laboratory. They were

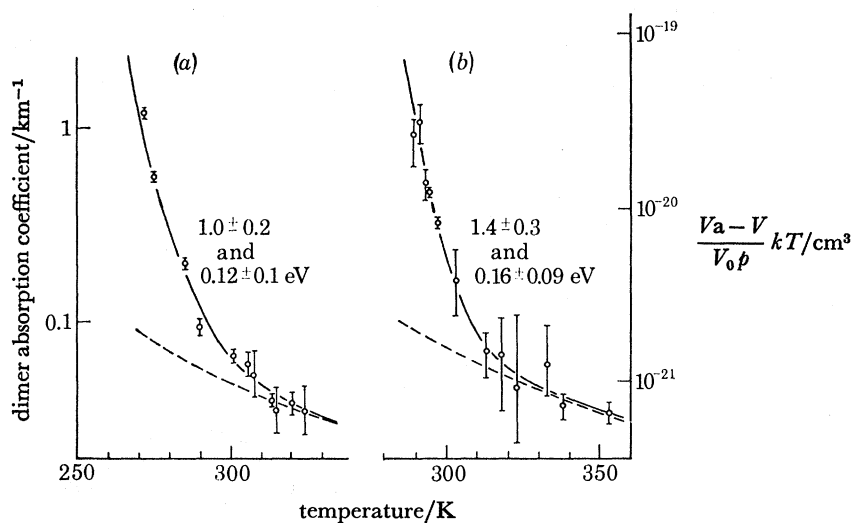


FIGURE 2. (a) Comparison of observations with expectation. The full line shows the temperature dependence of absorption (normalized to monomer concentration of  $10^{17} \text{ cm}^{-3}$ ) by the component which varies quadratically with water vapour pressure. The dotted line shows the behaviour of equilibrium water dimers. (b) Qualitatively similar behaviour to the absorption data of figure 2(a) but obtained from speed-of-sound observations (Bohlander & Gebbie 1975).

designed first to discriminate against monomer absorption by making measurements as far as was practicable from line centres to minimize the magnitude of the monomer component. The long absorption length requirements were met by the development of a new untuned cavity technique. Figure 2 gives results of measurements on water vapour near saturation for a wave-number of  $7.1 \text{ cm}^{-1}$ . The component of absorption having a quadratic dependence on water vapour pressure has been studied as a function of temperature and compared with the expected behaviour of equilibrium dimers. At low temperatures a much steeper dependence is found, which indicates that some other molecular complex is dominated in the absorption at  $7.1 \text{ cm}^{-1}$ . Though the exact physical interpretation of this remains to be made, it is plausible that it is related to the anomalous absorption observed in the real atmosphere. It also shows a steeper dependence on temperature than would be expected from water dimers in equilibrium. Such temperature behaviour is similar to what was found by speed of sound measurements shown in figure 2(b), which can be taken as effectively measuring the molecular mass. These are

interpreted as showing the presence of a non-equilibrium molecular complex which is distinct from the equilibrium dimer and which has a strongly temperature dependent relaxation time.

The other wavelength region where anomalous absorption has been observed is in the relatively transparent gap between 8 and 13  $\mu\text{m}$ . Here, however, it is necessary to make a clear distinction with loss that is directly attributable to condensed phase particles, but this can be done by making measurements in conditions where the visible region transparency is high. Such measurements using the temperature dependence criterion already mentioned have shown that an anomalous component can be the dominant source of opacity in the window region. It is emphasized that an important criterion for distinguishing a component of absorption, which may properly be attributed to water dimers in equilibrium, is its dependence on temperature. For equilibrium species this should be dominated by concentration changes which themselves are determined by the dimer binding energy, which is now well determined as about 0.16 eV per molecule. The failure to find that the observed temperature dependence in a number of real atmosphere measurements conforms to this result is valuable evidence for the existence of an anomalous component in addition to that which can be attributed to dimers.

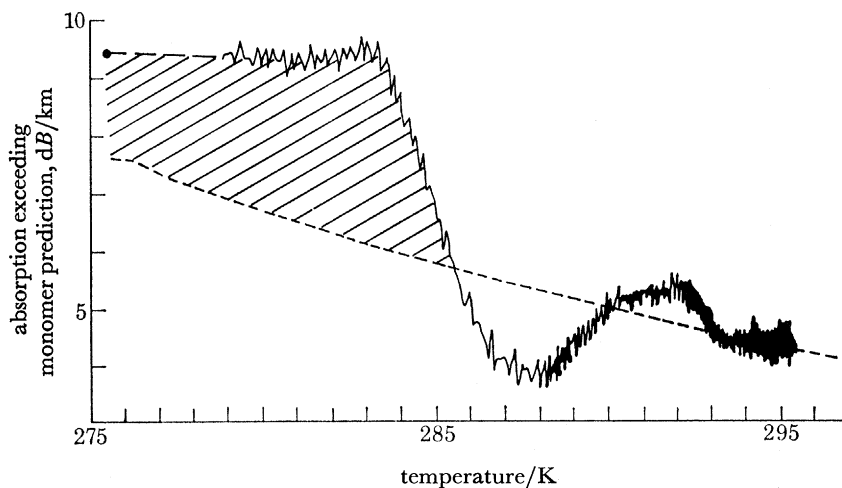


FIGURE 3. Comparison of absorption by water vapour subjected to an adiabatic expansion in a closed chamber (full line) with the expected behaviour if the only molecular component present in addition to monomers were equilibrium dimers with a binding energy of 0.16 eV per molecule (dotted line). The shaded area shows a delayed excess absorption related to supersaturation. The experiment used radiation in the 7–30  $\text{cm}^{-1}$  range where anomalies are observed in the atmosphere (see figure 1).

#### POSSIBLE RELATIONSHIP OF ANOMALOUS ABSORPTION AND SUPERSATURATION

The phenomenon of supersaturation is a well studied part of non-equilibrium behaviour of water vapour. The experimental facts established in the classic researches of C. T. R. Wilson and C. F. Powell were subsequently extended, but this was mostly in the direction of particle detection technology, and the underlying physics of supersaturation appears to have been remarkably neglected. With the conviction that anomalous absorption must also involve non-equilibrium states of water, it seemed that it would be profitable to see if supersaturation and anomalous absorption had any measurable characteristics in common. This has been done by applying adiabatic expansions to mixtures of water vapour and a carrier gas in a multipass cell and then making appropriate spectral absorption measurements. For technical reasons

connected with the use of interferometric spectroscopy, it is convenient to make the investigation in two stages. In the first, the time dependence of absorption is studied for a band of radiation covering the spectral region in which anomalous absorption has been observed. In the second stage, a knowledge of the time dependence of total absorption will be used to select the parts of the time cycle which are likely to show the biggest effects, and for these the spectrum will be measured. Here, only results of the time dependence of total absorption are given. Figure 3 shows a comparison of the observed absorption with the expected cell transmission calculated for a model of water vapour composed of monomers and equilibrium dimers. In essence, it is found that there is an extra component of absorption which lasts about one second or longer after the time when maximum supersaturation is reached. This is of the order of the time that supersaturation can be maintained in cloud chamber studies, and suggests that the desired connection between anomalous absorption and supersaturation has been demonstrated. There is, however, much greater complexity in the time behaviour than this simple picture suggests, and the second stage of deriving the successive spectra of the supersaturated vapour will be necessary before useful comment can be made since it is necessary to make a careful separation of dimer and anomalous components. It is already evident from experiments made on changing the spectral pass band that such a separation can be made.

## REFERENCES (Gebbie)

- Bohlander, R. A. & Gebbie, H. A. 1975 *Nature, Lond.* **253**, 523.  
Moffat, P. H., Bohlander, R. A., Macrae, W. R. & Gebbie, H. A. 1977 *Nature, Lond.* **269**, 676.