

Light-scattering experiments on water vapour at pressures approaching saturation

THE existence of dimers in water vapour at pressures approaching saturation has been postulated for some years and a number of observations have been interpreted in terms of them¹⁻⁴. The relative dimer concentration is expected to increase sharply with increasing percentage saturation and decreasing temperature^{1,3}. From speed of sound measurements, a dimer concentration of 8 parts per 10³ has been reported at 50 °C and 90% saturation³; this might be expected to increase to >20% at 95% saturation and 20 °C. It may be supposed that the polarisability of the water dimer will be considerably larger than that of the monomer, and therefore, using an assumed value for polarisability, an estimate of the dimer concentration at a given temperature and vapour pressure can be made by comparing the quadratic term in a plot of the light scattered as a function of pressure with the known second virial coefficient. In early experiments, using a large multi-pass scattering cell, a very large quadratic term was observed. This arose, however, largely from a rapid increase in the elastic scattering from water-contaminated surfaces as the vapour pressure in the cell approached saturation. We have now eliminated this spurious scattering by selecting spectroscopically only those photons which exhibit a frequency shift due to Brillouin and Raman scattering.

In these experiments two particular difficulties were found: elimination of parasitic light by spectral analysis leads to a large reduction of an already weak signal, and the peculiar problem of reliable pressure measurement with water vapour. Because of surface adsorption, the pressure changes considerably after charging a system with vapour. It was found that long periods, often >1 h, were required before 1% stability could be established in our cell. The consequently long experimental periods thus necessitated very good stability of optics and laser power and constancy of detector response. (For a discussion of high precision photon counting applied to light-scattering studies see ref. 5.)

In our experiments the beam from an argon ion laser (300 mW; 488.0 nm) was directed through a small cell, containing variable amounts of water vapour, and light scattered at 90° to the beam (containing Raman, Brillouin and Rayleigh components) was detected after passing through a confocal, piezo-electrically scanned, Fabry-Perot etalon of free spectral range 375 MHz and finesse ~ 60. The photon counts were registered in a multi-channel analyser. Frequency-shifted light,

scattered from the vapour, was selected by counting only photons between Rayleigh peaks. A reference beam, using the same collection system and detector served as a monitor from which small corrections could be made for fluctuations of laser power or detector sensitivity.

A representative set of results is shown in Fig. 1 with a least-squares quadratic fit to all data points up to and including the cluster of four observations close to 95% saturation vapour pressure (SVP). The parabola is of the form $S = aP + bP^2$ (where S = photon count and P = pressure) and we find the quadratic term (bP^2/aP) has the value of $2.2 \pm 1 \times 10^{-3}$ at 95% SVP. Values of the second virial coefficient B in water vapour, and its division between a van der Waals' component B_1 and a 'dimer' component B_2 , have been given in ref. 4. These suggest that at 95% SVP and 20 °C, $\sim 0.45 \times 10^{-3}$ of the quadratic scattering can be attributed to the increased concentration of monomers because of the van der Waals' attraction (B_1); the remainder $1.75 \pm 1 \times 10^{-3}$ must be attributed to scattering from dimers. The assumption that scattering from a dimer is twice that from the monomer leads to a fractional concentration of dimers of $0.88 \pm 0.5 \times 10^{-3}$ —an order of magnitude less than the earlier reported values³. On the other hand, the values of B_2 given in ref. 4 would suggest a fractional dimer concentration of only 0.82×10^{-3} at 20 °C and 95% SVP—a value supported by our light-scattering measurements. Alternatively, by adopting this latter value for the concentration, we can calculate the scattering from a dimer as 2.2 times that from a monomer—a figure which is probably quite reasonable in consideration of the likely polarisability of a linear or chain-like dimer⁷. Our experiment consisted of a search for small effects in quasi-elastic scattering, and its accuracy is limited by the peculiar problems of working with water vapour. It seems likely that a Raman scattering experiment should be more definitive, with the possibility of associating specific spectral features with the water dimers.

In conclusion, we note that Fig. 1 shows a number of readings at, and very close to, SVP. In these observations it is likely that significant condensation occurred in the cell, and that small (<0.2 °C) temperature fluctuations during each experiment contributed significantly to small pressure variations. Owing to the possibility of water droplet formation on the windows these results must therefore be interpreted with caution in spite of our monitoring technique. One might, however, expect relatively large concentrations of dimers and multimers at SVP and, as a consequence, the increased scattering which is observed.

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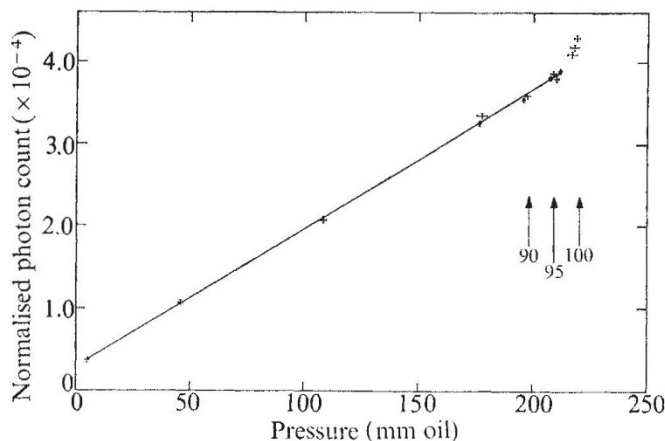
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Fig. 1 Variation of inelastic scattered light with water vapour pressure at 20.2 °C. A least-squares parabola (indistinguishable from a straight line at this scale) is fitted to the data points up to 95% SVP. Error bars indicate s.d. in photon counts and observed pressure variations. Arrows indicate % SVP.



Major magmatic activity as a key to predicting large earthquakes along the Sagami Trough, Japan

MIHARA-YAMA is a basaltic stratovolcano on Oshima, an island lying about 20 km off the coast of Izu Peninsula in central Japan (Fig. 1). I attempt here to show that the magmatic activity of Mihara-yama could be used to predict