The recent observation of the water dimer (H$_2$O•H$_2$O) has verified the presence of a new class of compounds in our atmosphere known as hydrated complexes.$^1$ These complexes consist of a water molecule weakly bound to another molecule.

Complexes, or clusters as they are sometimes called, are small assemblies of atoms or molecules held together by the weak van der Waals interactions. A simple example of a complex is the weakly bound He dimer (He•He). The binding energy between the He atoms arises from dispersion (or London) forces and is extremely small, ~10$^{-6}$ kJ/mol. This dimer (and larger He complexes) is formed in a jet expansion of He gas into a vacuum. The expansion cooling makes formation of the complex more favourable than otherwise. In recent years larger He complexes (liquid helium nanodroplets) have been used as a medium for spectroscopy. The droplets provide a unique environment that is ideally suited to the spectroscopic study of biomolecules, metal complexes, radical complexes, hydrogen bonded clusters, and ions, as the He droplet imparts only a minimal influence on the species embedded inside it.$^2$ Currently, this spectroscopic technique is not available in New Zealand.

Research on complexes has recently experienced an explosive growth and many examples involving not only various molecules and atoms, but also radicals and ions, have been observed in laboratories.$^3$ An early example was that of an Ar atom weakly bound to the p-electron cloud of an aromatic ring (Fig. 1). The vibrational frequency of the trampoline vibration of the Ar atom has been measured and used to determine the binding energy. This type of interaction is typically very weak with binding energies ~2-4 kJ/mol. More recently, an interesting class of complexes has been studied that involve functionalised alkanes binding to p-electrons, as shown by the chloroform-benzene complex, CHCl$_3$•C$_6$H$_5$.$^4$ Complexes that involve dipole-dipole interactions, such as traditional hydrogen bonds, are much stronger. The phenol dimer (Fig. 2) is one example. Binding energies in these types of complexes are typically about 20 kJ/mol. The atoms involved in hydrogen bonding (O • • • H–O) prefer to align in a near-linear arrangement, with an inter-oxygen distance of about 3 Å.

Complexes between water and an acid are usually even stronger. In addition to one strong hydrogen bond, a second partial hydrogen bond is often formed. The partial hydrogen bond is characterised by a non-linear arrangement and a longer inter-oxygen distance. One example is the water-sulfuric acid complex, H$_2$O•H$_2$SO$_4$ (Fig. 3) and binding energies of these water-acid complexes are about 40 kJ/mol.$^{5,6}$ Some of the strongest complexes are cyclic, such as the formic acid dimer shown in Fig. 4. In these complexes there are two equivalent and cooperative strong hydrogen bonds and the total binding energy is as high as 60 kJ/mol.

In general, the formation of complexes can significantly change the physical and chemical properties of the individual parent molecules. Hydrogen bonding significantly alters the frequency of the infrared (IR) fundamental vibrational transitions of the OH bond involved.$^7$ It typically leads to a lower frequency (red-shift) and a higher intensity of the fundamental OH-stretch of the hydrogen donor.

Recently, examples have been found in which a frequency shift to blue occurs upon complexation. The fundamental CH-stretching vibration in the chloroform-benzene complex is shifted about 15 cm$^{-1}$ higher than the CH-stretching transition in free CHCl$_3$.$^4$ This blue shift is small in comparison to the dramatic red-shift (500 cm$^{-1}$) found for the OH-stretching vibration in nitric acid upon formation of the strong hydrogen bonded water-nitric acid complex, H$_2$O•HNO$_3$.$^{5,8}$ The blue shift observed in the chloroform-benzene complex resulted in the interaction being labelled an anti-hydrogen bond.$^4$

The formation of complexes also has the ability to significantly change reaction rates, as was demonstrated a decade ago for the hydration of sulfur trioxide.$^9$ Calculation showed the reaction to be second order with respect to water pressure, and involved the formation of a water-sulfur trioxide, H$_2$O•SO$_3$ complex, in qualitative agreement with the experimental rates.$^{10}$

These examples suggest that hydrated complexes in our atmosphere can impact on the spectroscopy and chemistry. Complexes can change the ability of parent molecules to absorb both solar and terrestrial emissions. In addition they can provide access to completely new ways by which reactions occur, which could have a significant effect on
atmospheric chemistry. A better understanding of these complexes would facilitate an improved modelling of weak interactions that are important in many areas of chemistry. The focus of this article is the spectroscopy of the water dimer, its detection in the atmosphere, and the effect that it has on the atmospheric absorption of solar radiation.

The water dimer: structure, spectroscopy, and atmospheric detection

The structure of the water dimer was determined by microwave spectroscopy using isotopic substitution effects, the Stark effect, and measurements of the hyperfine structure. The equilibrium structure of the water dimer has $C_s$ symmetry and is shown in Fig. 5. The complex consists of an acceptor unit (H$_2$O$^+$) and a donor unit (H$_2$OH) with a binding energy of 20 kJ/mol. The structure is consistent with a near-linear hydrogen bond with an experimentally determined inter-oxygen distance of 2.98 Å. The structure deduced from the measurements is in excellent agreement with that predicted by ab initio calculations. The OH bond involved in hydrogen bonding (OH$_b$) is about 4 mÅ longer than the OH bonds in the water monomer. The OH bonds of the acceptor unit (OH$_a$) are close in length to those of the water monomer, and slightly longer (1 mÅ) than the free OH bond on the donor unit (OH$_f$). Based upon the structural parameters we would expect the vibration associated with the longer OH$_b$ bond to be significantly red-shifted.

It is a challenging task to observe these complexes experimentally because of predominantly low concentrations in water vapor and the strong absorbance by the water monomer that limits studies to fundamental vibrational transitions in the IR region. Most experiments have relied upon supersonic expansion techniques to provide a reasonable abundance of complex. The jet expansion technique generates not only the dimer but also larger water complexes in ratios that depend on the particular jet conditions; the spectra of the different complexes are difficult to separate. Huisken et al. used crossed molecular beams to record spectra of size-selected water complexes and found two transitions in the IR spectrum of the dimer that correspond to the fundamental OH-stretching transitions of the bonded OH$_a$ and free OH$_f$ oscillators. Previously, rotationally resolved spectra of the asymmetric OH-stretch of the acceptor unit had been reported. Recently, matrix isolation techniques have been used to record the vibrational spectrum of the water dimer up to 7300 cm$^{-1}$ and provided valuable information on the fundamental and first overtone OH-stretching transitions, whereas vapour phase spectroscopy of the dimer has so far been limited to fundamental transitions. However, an inherent problem with matrix isolation spectroscopy is perturbation from the matrix, which usually gives rise to frequency and intensity shifts relative to vapour phase spectra.

To determine the effect of the water dimer on absorption of solar radiation, the frequencies, intensities, and line widths of its vibrational overtone transitions in the near infrared (NIR) and visible (vis) regions must be known. We have developed a unique theoretical model that has allowed us to calculate the vibrational spectra of complexes from first principles. The NIR/vis spectra of molecules that contain OH bonds are dominated by transitions involving OH-stretching overtones. These overtone transitions are described well by the local mode model of molecular vibration, and we use the harmonically coupled anharmonic oscillator (HCAO) local mode model to describe the OH-stretching vibrations in the water
Each water unit in the dimer is modelled as two harmonically coupled anharmonic (Morse) OH-stretching oscillators. We have extended this HCAO local mode model to include the HOH-bending modes. The other vibrational modes in the water dimer have vibrational frequencies of the order of 100 cm$^{-1}$ and contribute very little to the overtone intensities.

Solution of the Schrödinger equation associated with the HCAO local mode model Hamiltonian leads to vibrational energies and wavefunctions. In the hydrogen acceptor unit the two OH bonds are equivalent and the vibrational states are labelled as the symmetrized $|v0\rangle_S$. For the fundamental vibrations ($v=1$) these two states would be similar to the well known symmetric ($v_1$) and antisymmetric ($v_2$) vibrations in the water molecule. In the donor unit the two OH-stretching oscillators are non-equivalent and the vibrational states are labelled $|v\rangle_f$ or $|0\rangle_f$ corresponding to having the vibrational energy in one of the two bonds.

Our calculated spectrum of the fundamental OH-stretching transitions in the water dimer is shown in Fig. 6, where it is compared with the three transitions observed in the molecular beam experiments. The calculation predicts the lowest energy peak, associated with the hydrogen bonded OH$_b$ $|1\rangle_b|0\rangle_f$, to be the most intense transition in the fundamental region. The symmetric stretch of the acceptor unit is calculated to be the weakest transitions, and is not observed in the molecular beam experiments. The calculated frequencies are within 10 cm$^{-1}$ of the experimental values for each of the three observed transitions. In matrix isolation experiments, the interactions between the matrix and the water dimer cause frequency shifts of up to 50 cm$^{-1}$ for a nitrogen matrix and up to 25 cm$^{-1}$ for an argon matrix.

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The molecular beam experiments do not provide intensity information and thus we use matrix isolation results to verify our calculated intensities. Fig. 7 shows the calculated intensities of the four fundamental OH-stretching transitions in the water dimer compared to relative intensities obtained from N$_2$ and Ar matrix isolation experiments. Not surprisingly, the intensity of the strong $|1\rangle_b|0\rangle_f$ transition has been set to 100 to facilitate comparison. The intensity pattern in the acceptor unit is, very similar to that of water monomer, with the asymmetric transition $|10\rangle_-$ significantly stronger than the symmetric transition $|10\rangle_+$. In the donor unit the hydrogen bonded transition $|1\rangle_b|0\rangle_f$ is stronger than the free OH-stretching transition $|0\rangle_b|1\rangle_f$, as is commonly observed for hydrogen bonds.

Fig. 8 shows a similar comparison for the four pure local mode transitions in the first OH-stretching overtone. The two transitions from the acceptor unit, $|20\rangle_-$ and $|20\rangle_+$, have similar relative intensities to those in the fundamental region, and in terms of absolute intensity show the typical order of magnitude decrease. The intensity of the free OH-
transitions in the OH-stretching third overtone region. In contrast, the hydrogen bonded transition \( |2\rangle_f \leftarrow |0\rangle_f \) shows a remarkable four orders of magnitude drop in intensity, and matrix isolation experiments have so far have failed to observe this transition. This unexpected intensity decrease can be explained by cancellation of terms in the expansion of the dipole moment function, as detailed elsewhere.\(^{22}\)

The comparison of our calculated spectra with those from molecular beam and matrix isolation clearly illustrates that the calculations are sufficiently accurate to be useful as a guide to further laboratory studies, as well as to facilitating atmospheric detection of the water dimer. The main difficulty with atmospheric detection is overlap with water monomer bands, which have broad rotational envelopes. Fig. 9 shows the calculated spectrum of the water dimer in the third OH-stretching overtone region compared with the rotational resolved water monomer spectrum.\(^{21}\) The hydrogen bonded OH-stretching transition \( |4\rangle_f \leftarrow |0\rangle_f \) is sufficiently red-shifted from the water monomer lines and is predicted to have sufficient intensity to allow its detection.

Last year this water dimer overtone transition was measured by atmospheric long-path (18.34 km) differential optical absorption measurements in the air above the North-Sea; it was the first observation of the water dimer in the Earth’s atmosphere.\(^{1}\) Guided by our calculations, a 19.4 cm\(^{-1}\)-wide Lorentzian-shaped band was detected at 749.5 nm (13,340 cm\(^{-1}\)) as predicted by us at 13,400 ± 100 cm\(^{-1}\). Prior to our calculations, experimentalists were focusing on different spectral regions.\(^{21}\) The intensity of the observed band showed a dependence on \([\text{H}_2\text{O}]^2\) as expected for a water dimer transition. The atmospheric abundance of the water dimer was estimated by comparison of our calculated oscillator strength and the measured intensity of this transition.\(^{24}\) The abundance depends on temperature and water concentration but is about one water dimer per 1000 water molecules.\(^{24}\)

Our calculated spectrum of the water dimer has allowed an evaluation of its impact on the absorption of solar radiation in the atmosphere. The water monomer absorbs radiation in sharp rotationally resolved lines whereas the water dimer bands are broader and often frequency shifted. Line-by-line radiative transfer simulations of absorption of solar radiation have found that the contribution from the water dimer depends significantly on the line shape of the transitions, but is ~1% of the total absorption of solar radiation.\(^{25,26}\) The importance of the line-shape on these simulations demonstrates the need for further laboratory spectra of the water dimer in atmospherically relevant conditions.

We have found that the water dimer is likely to constitute a large fraction of the empirical continuum currently used to explain discrepancies between observed and modelled radiative transfer.\(^{25,27,28}\) It is also likely that other hydrated complexes, such as \(\text{H}_2\text{O}^+\text{N}_2\) and \(\text{H}_2\text{O}^+\text{O}_2\), play an important role in radiative transfer.\(^{26}\) These hydrated complexes could also affect the absorption of terrestrial emission and hence have an impact on global warming.\(^{27}\)

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