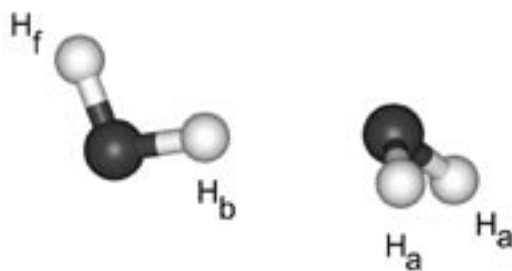


# Overtone Spectroscopy: A Sensitive Probe of Hydrogen Bonding

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Hydrogen bonded complexes in the Earth's atmosphere recently have been shown to be of potential importance to climate change.<sup>1,2</sup> These complexes are generally held together by a weak hydrogen bond as shown in Fig. 1 for the water dimer,<sup>3</sup> and are difficult to study under conditions relevant to the atmosphere. So far only the water dimer and the van der Waals complexes, the molecular oxygen dimer ( $O_2 \cdot O_2$ ) and the dimer between molecular oxygen and molecular nitrogen ( $O_2 \cdot N_2$ ), have been observed in the atmosphere or under atmospheric conditions.<sup>4-7</sup> One of the key questions regarding hydrogen bonded complexes is how their spectroscopy affects the absorption of solar radiation in the near infrared (NIR) and visible wavelength regions. The near infrared region is dominated by low-lying electronic transitions and vibrational overtones of XH-stretching transitions ( $X =$  any heavy atom). Although there are no distinct boundaries for the near infrared region, typically it is considered to lie within 4000-14,000  $cm^{-1}$ . The calculated changes in absorbance of hydrated complexes  $H_2O \cdot M$ , ( $M$  is a molecule present in the atmosphere) in the NIR and visible regions have supported the suggestion<sup>8-10</sup> that the complexes are part of the explanation for the so called water vapour continuum, an empirical continuum used in radiative transfer modeling.<sup>11-13</sup>



**Fig. 1.** The structure of the hydrogen bonded water dimer; the  $OH_b$  bond length is elongated due to the presence of the other water molecule.

The equilibrium constants for hydrogen bonded complexes in the vapour phase are typically small, which makes their study difficult. Consequently, our attention has been directed to the spectroscopy of molecules with internal hydrogen bonds. There are some infrared studies of hydrogen bonded systems in the vapour phase, however studies in the overtone regions are very limited.<sup>14</sup> One reason for the lack of study is that overtone transitions are inherently weak. Their intensity typically drops by an order of magnitude with each successive quantum of vibrational excitation. Another reason is that many species that undergo hydrogen bonding have relatively low vapour pressures, so low sample concentration is an issue. To overcome these hurdles, one or a combination of conditions such

as long sample path lengths, high temperatures, or sensitive spectroscopic techniques are required. One sensitive technique is intracavity laser photoacoustic spectroscopy.

## Intracavity photoacoustic spectroscopy

The photoacoustic effect was serendipitously discovered by Alexander Graham Bell in 1880 when he observed that an audible sound is produced when modulated sunlight is incident on an optically absorbing material.<sup>15</sup> Photoacoustic spectroscopy can be categorized as a photocalorimetric or photothermal technique, since it measures the internal heating of a sample due to the absorption of radiation. When a sample is illuminated with modulated monochromatic light, and if some of that light is absorbed by the sample, internal energy levels within the sample are excited. Subsequent de-excitation (relaxation) of the excited states results in all or part of the absorbed energy being transformed into heat energy through nonradiative decay processes. Since the incident light is intensity modulated, the internal heating of the sample is also modulated. This modulated heating creates pressure waves that are detected as sound by a microphone. Modern microphones and related electronic devices are capable of detecting pressure waves caused by temperature rises as low as  $10^{-6}$  °C in gaseous samples.<sup>16</sup> We use microphones that were originally designed for hearing aids.

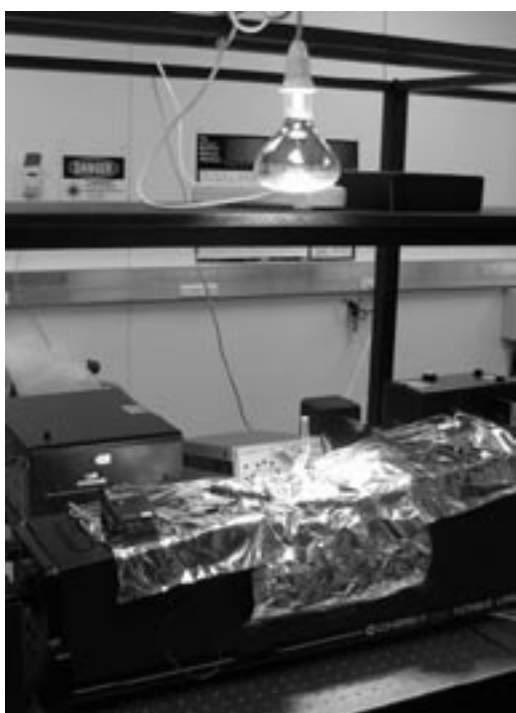
There are several advantages of photoacoustic spectroscopy over conventional spectroscopy. Since absorption of light by a sample is required before a photoacoustic signal is produced, light that is elastically scattered or transmitted is not detected, and consequently it does not interfere with the intrinsically absorptive photoacoustic measurement. Thus photoacoustic spectroscopy can be considered as a zero noise background technique, and this sensitivity allows for the study of trace amounts of species or species with weak absorptivities. The use of high-powered tunable lasers, such as a titanium:sapphire laser and a dye laser as in our photoacoustic spectrometer, makes this technique very sensitive. The dye and titanium:sapphire lasers of our photoacoustic spectrometer are shown in Figs. 2 and 3.

As mentioned, the vapour pressure of a hydrogen-bonded species is typically low. The vapour pressure of the sample can be increased with heating. We have used a 250 watt heat lamp suspended over the photoacoustic cell to conduct variable temperature photoacoustic experiments. A photograph of this setup is shown in Fig. 3. The temperature can be simply varied by altering the distance of the lamp to the cell. The location around the cavity of the titanium:sapphire laser where the photoacoustic cell is placed is lined with aluminium foil to reflect heat. The foil has an extra role as a dust cover for the laser as the normal

one could not be used during a heating experiment. This heating method has proved quite effective, for temperatures up to 60 °C, with the temperature remaining within  $\pm 1$  °C during a typical 2 h scan. The vapour pressure increases exponentially with temperature so even a small temperature increase has a significant effect on the vapour pressure. Recently, using our photoacoustic spectrometer, we have recorded vapour phase overtone spectra of compounds that are solids at room temperature.



**Fig. 2.** The dye laser of a photoacoustic spectrometer in operation; the cavity of the laser extends from the bright spot (front) along the visible beam and the sample cell is housed in it.



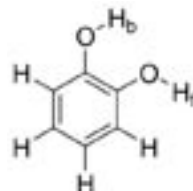
**Fig. 3.** Heating lamp suspended over a titanium:sapphire laser; the photoacoustic cell is in the laser cavity with its glass tip pointing towards the heat lamp.

### Intramolecular hydrogen bonding in overtone spectra

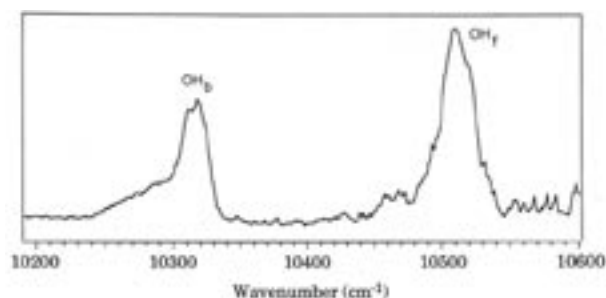
There are only a few cases of vapour phase overtone spectra of molecules that are solids at room temperature and these include phenol<sup>17</sup> and naphthalene<sup>18,19</sup> with room temperature pressures of about 0.35 Torr and 50 mTorr, respectively. Herein we present our recent vapour phase overtone spectra of catechol (1,2-dihydroxybenzene) and ethylene glycol (1,2-ethanediol), both molecules with

room temperature vapour pressures of a few mTorr.<sup>20,21</sup> The NIR/vis spectra of molecules containing OH bonds are dominated by transitions that involve OH-stretching overtones. These overtone transitions are described well by the local mode model of molecular vibration,<sup>22,23</sup> where each of the non-equivalent OH bonds is described by an isolated anharmonic oscillator, typically the Morse oscillator. We have developed a theoretical model that allows calculation the vibrational overtone spectra from first principles.<sup>21,24,25</sup>

Catechol contains an intramolecular hydrogen bond between the two OH bonds as shown in Fig. 4. The hydrogen bond angle (O-H<sub>b</sub>•••O) in catechol is that of a quasi-five-membered ring, far from an optimal linear conformation.<sup>26</sup> Thus the intramolecular hydrogen bond in catechol is expected to be weak. The second OH-stretching overtone spectrum of catechol vapour is shown in Fig. 5. Two distinct peaks are observed in the room temperature intracavity laser photoacoustic spectrum of catechol corresponding to the *free* and *bonded* OH bonds (labelled OH<sub>f</sub> and OH<sub>b</sub>). The weak intramolecular hydrogen bonding stretches the OH<sub>b</sub> bond by about 0.4 pm.<sup>20</sup> It is clear from Fig. 5 that this small change in the OH bond length leads to a large and easily observable frequency shift of the associated vibrational overtone transition. The shift in frequency increases with vibrational excitation making it desirable to record higher overtones. However, as mentioned above, the intensity of these overtone transition decreases with vibrational excitation. This overtone spectrum of catechol can also be recorded at very cold temperatures (1 K) under jet conditions with a technique called *non-resonant ionization detection*.<sup>27</sup> This has the advantage of producing narrow band widths of a few wave numbers and makes it possible to observe even smaller changes in the OH bonds. By combining overtone spectroscopy and the jet cooled technique we have been able to resolve conformational isomers in *m*-aminophenol, where the calculated bond length difference is less than 0.002 pm.<sup>28</sup>



**Fig. 4.** Catechol is planar with two distinct OH bonds.



**Fig. 5.** Intracavity laser photoacoustic spectrum of vapour phase catechol in the 3 quanta of OH-stretch (second overtone) region; the OH<sub>b</sub> stretching second overtone is at 10320 cm<sup>-1</sup> and that for the OH<sub>f</sub> stretching is at 10500 cm<sup>-1</sup>.

Ethylene glycol is one of the simplest molecules with two vicinal OH groups, and it can serve as a simple model for biological molecules such as sugars. Similar to catechol, the conformation of the intramolecular hydrogen bond in ethylene glycol comprises of a five-membered ring. It is a triple rotor molecule that can exist in one of 27 ( $3^3$ ) conformations. Some of the structures are degenerate due to symmetry and the number of unique conformations is reduced to 10. Of these 10, the 2 most stable contain an intramolecular hydrogen bond (Fig. 6) with conformer 1 favoured over conformer 2 by approximately 2 kJ mol<sup>-1</sup>. The remaining 8 structures are predicted to have significantly lower populations.<sup>21,29</sup>

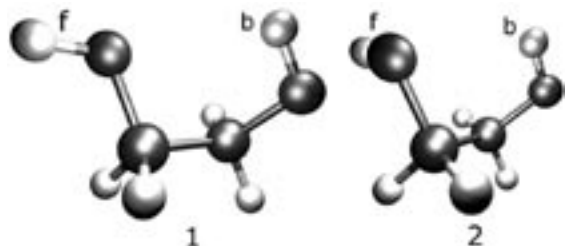


Fig. 6. The two most stable structures of ethylene glycol.

The vapour phase OH-stretching spectra of ethylene glycol in the 2<sup>nd</sup> to 4<sup>th</sup> overtone regions are presented in Fig. 7. The abscissa of each overtone region is 550 cm<sup>-1</sup> wide to illustrate the typical spreading apart of the transitions with increasing vibrational excitation. In these higher overtone spectra, it is possible to identify the transitions from the two lowest energy structures. We have labelled the OH<sub>b</sub> and OH<sub>f</sub> stretching transitions of structures 1 and 2 as 1b/2b and 1f/2f, respectively. The bonded transitions are observed to undergo a red shift relative to the free transitions, indicative of the presence of hydrogen bonding.

Our experimental work as illustrated by the spectra of catechol and ethylene glycol is complemented with theoretical studies. We use the local mode model of molecular vibration mentioned before to model the OH-stretching overtone transitions using high level ab initio quantum calculations to solve the electronic Schrödinger equation. Potential energy and dipole moment curves are obtained and these make it possible to calculate the frequencies and intensities of the vibrational overtone transitions. The calculated accuracy is highly dependent on the level of the ab initio method applied to the molecule. Recently, we found that with *high level coupled cluster* methods it is possible to obtain accurate predictions of the frequency ( $\omega$ ) and anharmonicity ( $\omega x$ ) of the anharmonic local mode oscillator. The experimental and calculated frequencies and anharmonicities of the lowest energy conformer of ethylene glycol are given in Table 1 (The data are obtained from a potential energy curve calculated with the coupled cluster theory including singles doubles and perturbative triples (CCSD(T)) combined with Dunning's augmented triple zeta (aug-cc-pVTZ) basis set<sup>21</sup>). The agreement between calculated and observed local mode parameters is excellent. This makes it possible to calculate accurate spectra of molecules that have not previously been observed.

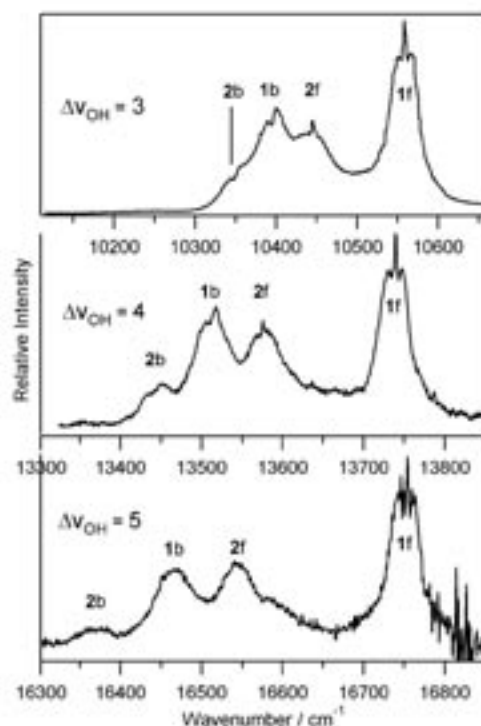


Fig. 7. Photoacoustic spectra of ethylene glycol vapour in the 3 to 5 quanta of OH-stretch regions; the *bonded* and *free* transitions of the two most stable structures are labelled.

Table 1. Observed and CCSD(T) calculated OH-stretching local mode parameters (in cm<sup>-1</sup>) for the lowest energy conformer of ethylene glycol.

	1b		1f	
	$\omega$	$\omega x$	$\omega$	$\omega x$
Calc.	3806	82.9	3856	84.1
Expt.	3803	85.1	3856	84.3

The level of accuracy possible with the CCSD(T) method alleviates the need for empirical scaling often used in connection with the calculation of vibrational frequencies. The downside of the method is that it is computationally demanding, easily requiring months of computer time even with today's fastest computers!

Contrary to the usual red shift of vibrational frequencies observed for hydrogen bonds, there has been evidence found for a blue-shifting intramolecular hydrogen bond in the overtone spectrum of 1H-nonafluorobutane.<sup>30</sup> The molecule is shown in Fig. 8. In this case, a weak intramolecular hydrogen bond is formed between the hydrogen and a fluorine atom.

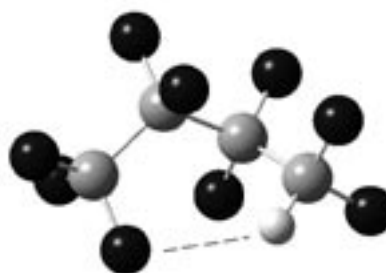


Fig. 8. The structure of 1H-nonafluorobutane with the proposed hydrogen bond.

Efforts are underway at Otago University to record overtone spectra of species undergoing even stronger hydrogen bonding and to observe effects of the aromatic ring  $\pi$  cloud on hydrogen bonding.

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