4. Absorption spectroscopy theory

Spectroscopy describes the interaction of electromagnetic radiation with atoms or molecules. The theoretical base that has been developed to explain this process is voluminous, however it is possible to consider a manageable portion of the theory by focusing on aspects that relate directly to the measurement we want to perform. This means restricting the focus of this chapter to a short outline of the rotational–vibrational spectroscopy of water vapour.

The theoretical background provides an indication of how the measurement is possible and also suggests what the limitations of an optical diagnostic technique based on spectroscopy may be.

The overview presented here is necessarily brief. Molecular energy levels that give rise to the absorption lines that are probed in this study are discussed first, along with the convention followed for labelling the transitions. Following this, aspects of the theory required for making a physical measurement are covered, including the prediction of line strength and line shape. This is used to determine how a measurement of absorption can be used to determine temperature and number density.

4.1 Molecular ro-vibrational energy levels and absorption lines

When a molecule absorbs a photon, its state must change to reflect the energy it has gained. The energy of the photon determines what aspect of the molecule's state is changed—the electronic configuration, the vibration state, the rotation state or some combination of these may change when a photon is absorbed.

The possible states that a molecule can be in are defined by quantum mechanical considerations, and the energy levels associated with these states are quantised. To be absorbed, the energy of a photon must equal the difference between two states, so it follows that absorption may only occur at particular frequencies

\[ \nu = \frac{E' - E''}{h} \]  

(4.1)

where \( E' \) and \( E'' \) are the energies associated with the upper and lower states respectively and \( h \) is Planck's constant. Following one of the conventions used in spectroscopy, the units used for \( \nu \) in this thesis are the wavenumber \([\text{cm}^{-1}]\) which is the inverse of the vacuum wavelength, and \( 1 \text{ cm}^{-1} \approx 30 \text{ GHz} \). Also by convention, the energy levels are written in equivalent frequency so that \( h \) can be removed from equation (4.1).
4. Absorption spectroscopy theory

Although not important for this work, it is worth noting that the line position varies slightly as pressure changes due to the change in the energy level of the molecule in the presence of collisions.

In the infrared region of the electromagnetic spectrum, light interacting with molecules results in changes in the rotational–vibrational state of the absorbing molecules. In the case of water vapour, the energy levels of these states can be enumerated by assigning three vibrational quantum numbers ($v_1, v_2, v_3$) and three rotational quantum numbers ($J_{K_a,K_c}$).

The vibrational quantum numbers relate to the modes of vibration shown in figure 4.1. They can take the values $0, 1, 2, \ldots$ and have energy spacings that mean that pure vibrational transitions are seen in the infra-red.

The general form of the rotational quantum numbers is set by the symmetry properties of the H$_2$O molecule. Since each of the three moments of inertia are unique, the molecule is classified as an asymmetric-top. For this class of molecule, there are several ways of characterising the rotational quantum numbers and the form used here is the same as reported in reference [114], which is a major source of line strength data for this work. Other systems for labelling the quantum numbers are $J_{K_a,K_c-1}$ or $J_{K_a,K_c+1}$ where $K_a$ and $K_c$ are pseudo-quantum numbers which serve as labels for the different energy within a particular $J$ level. The $\tau$ form simply orders the energy levels while $K_a$ represents the approximate projection of $J$ along the axis with the smallest moment of inertia and $K_c$ represents the approximate projection of $J$ along the axis with the largest moment of inertia [19].

The reason for this variation stems from the physical interpretation of these quantum numbers. $J$ is a good quantum number, in the technical sense, and represents the total angular momentum of the rotating molecule. In contrast, $K_a$ and $K_c$, or their alternate representations, are pseudo-quantum numbers which serve as labels for the different energy within a particular $J$ level. The $\tau$ form simply orders the energy levels while $K_a$ represents the approximate projection of $J$ along the axis with the smallest moment of inertia and $K_c$ represents the approximate projection of $J$ along the axis with the largest moment of inertia [19].

The spacing of rotational energy levels is much finer than the spacing of vibrational energy levels, compared diagrammatically in figure 4.2. Pure rotational transitions are observed in the microwave region of the electromagnetic spectrum however ro-vibrational transitions, where both the vibrational and rotational state changes during a transition, have energy separations that appear in the infra-red. Ro-vibrational transitions were probed in this study, which require the specification of the upper and lower vibrational and rotational quantum numbers to uniquely identify a transition.
4.2. The relationship between line and gas properties

The ro-vibrational energy levels of a molecule determine the frequency at which absorption lines will be present. However, in order to extract temperature and mole fraction information, we also need to know the strength and shape of particular absorption lines.

In reflection of our aim, it is convenient to present the supporting theory in terms of an absorption measurement with the general arrangement shown in figure 4.3.

As a monochromatic laser beam passes through a homogeneous medium, the transmitted intensity of the beam, \( I \), is related to the initial intensity, \( I_0 \), by the
Beer–Lambert relation

\[ I = I_0 \exp(-k_\nu l), \quad (4.2) \]

where \( k_\nu \) is the frequency-dependant absorption coefficient and \( l \) is the length the beam travels through the absorbing medium. The product \( k_\nu l = \log(I_0/I) \) is termed the spectral absorbance and this is the quantity that is measured in an experiment. Since \( l \) is simple to measure, \( k_\nu \) can be found.

If we consider the attenuation of the beam to be due to water vapour present in the test medium and we are in the neighbourhood of the \( i \)th absorption line, which is sufficiently isolated from other spectral features, then \( k_\nu \) is a function of the strength, \( S(T) \), and shape, \( g(\nu) \), of the absorption line and the number density, \( N_{H_2O} \), of water vapour. This relationship is given by

\[ k_\nu = S(T)g(\nu)N_{H_2O}. \quad (4.3) \]

So \( k_\nu \), as well as depending on frequency, depends on temperature, \( T \). The line shape function, \( g(\nu) \), is normalised so that \( \int g(\nu) \, d\nu = 1 \). Where we are interested in a wavelength region with multiple absorption lines, \( k_\nu \) can be treated as a sum over the individual absorption lines, i.e.

\[ k_\nu = N_{H_2O} \sum_i S_i(T)g_i(\nu). \quad (4.4) \]

If we are able to determine \( k_\nu \) over a sufficient frequency range \([\nu_1, \nu_2]\), so that \( \int_{\nu_1}^{\nu_2} g(\nu) \, d\nu \approx 1 \), and there is only one absorption line contributing to \( k_\nu \) over this frequency range, then equation (4.3) leads to

\[ N_{H_2O} \approx \frac{\int_{\nu_1}^{\nu_2} k_\nu \, d\nu}{S(T)}. \quad (4.5) \]

Therefore, number density of water vapour can be found provided that the strength of the absorption line is known. This requires knowledge of the temperature, since line strength is a function of temperature. Also possible is to choose an absorption line which has a small variation in strength over the expected temperature range.

An alternative to taking an integral of the measured absorbance is to fit a theoretical line shape to the measured data. This requires a choice of line shape function, which is discussed below. Despite being computationally intensive, which could be a major consideration for a real-time sensor, this method generally provides better results than taking a direct integral of the data. Furthermore, fitting is the only way of extracting the contributions of individual lines in regions where multiple spectral lines overlap. Temperature still needs to be specified in order to determine number density, however, but this need not be from an independent measurement. Instead, temperature can be found directly from absorption measurements due to the the way in which the strength of different absorption lines depends on temperature.
4.2. The relationship between line and gas properties

Strength of absorption lines

While some headway into the determination of absorption line parameters can be made directly from quantum-mechanical models of water vapour, the theory is not sufficiently advanced to give accurate results [19, 113]. A far more practical approach is available due to the existence of spectral databases such as HITRAN [97, 98] and reports of observed line strength such as Toth’s [114]. Rather than deriving expressions for line strength and other parameters from scratch, the HITRAN database tabulates line position and strength at a reference temperature and pressure, along with parameters that are used to scale strength at a reference temperature to any other temperature. HITRAN also includes line shape parameters, so that a relatively simple model can be used to reconstruct spectra at arbitrary pressure and temperature.

To scale the tabulated strength at temperature $T_0$, $S(T_0)$, to strength at an arbitrary temperature, $T$, we can use the expression [97]

$$S(T) = S(T_0) \frac{Q(T_0)}{Q(T)} \exp \left( -c_2 \frac{E''}{T} \right) \frac{1 - \exp \left( -c_2 \nu_0 / T \right)}{1 - \exp \left( -c_2 \nu_0 / T_0 \right)}.$$  \hspace{1cm} (4.6)

This scaling function depends on the lower-state energy of the transition, $E''$, the frequency of the transition, $\nu_0$, and the total internal partition sum of the molecule, $Q$. Also appearing in the expression is the second radiation constant, $c_2 = \hbar c / k$ where $\hbar$ is Planck’s constant, $c$ is the speed of light and $k$ is Boltzmann’s constant.

The partition function for a species at temperature $T$ can be written as

$$Q(T) = \Sigma_i g_i \exp \left( -E_i / kT \right),$$  \hspace{1cm} (4.7)

where $E_i$ is the $i$th energy level and $g_i$ is the degeneracy of the $i$th level. For this work, the partition function was computed numerically using the method of Fischer et al. [34]. In equation (4.6) the ratio $Q(T_0) / Q(T)$ in conjunction with the next term represents the change in the lower-state population with temperature, as demanded by the Maxwell–Boltzmann distribution. The final term is due to the effect of stimulated emission.

By measuring the strength of two lines we can measure temperature. From equation (4.6), we see that if we choose two spectral lines of different $E''$ and which are close spectrally (i.e. $\nu_0$ is similar for both lines) then the ratio of line strengths

$$R_{ls}(T) \equiv S_1(T) / S_2(T) = \frac{S_1(T_0)}{S_2(T_0)} \exp \left[ -c_2 \left( E_1'' - E_2'' \right) \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]$$  \hspace{1cm} (4.8)

is a function only of $T$. Then, knowing $T$, we can use equation 4.3 to determine $N_{\text{H}_2\text{O}}$. Therefore, if an experimental system is arranged in such a way so as to measure the integrated spectral absorption of two spectral lines with different lower-state energies then both temperature and species concentration can be deduced. Furthermore, the sensitivity of the thermometry can be tuned to a particular temperature range by choosing spectral lines with appropriate
$E''$. To find the relative sensitivity, $\frac{dR_l}{dT}/R_l$, we can differentiate equation (4.8), following Zhou [129], so that

$$\left| \frac{dR_l}{dT}/R_l \right| = c_2 \frac{|E_1'' - E_2''|}{T}. \quad (4.9)$$

If the relative sensitivity is below 1, errors in the determination of $R_l$ couple into larger relative errors in $T$, so high sensitivity is desirable. Maximising $|E_1'' - E_2''|$ is good for sensitivity but transitions with hugely different $E''$ have their peak line strengths at very different temperatures, meaning that if one of the two lines is visible then chances are good that the other is too weak to detect. This implies a trade-off between large $|E_1'' - E_2''|$ and the selection of lines that are strong enough to detect over the target temperature range.

A further implication of this equation is that the relative sensitivity decreases as a factor of $1/T$ meaning that any temperature measurement based on this technique will be more difficult to implement at higher temperatures. Beyond the temperature at which it peaks, the line strength of a particular transition heads towards zero faster than $1/T$, so weak absorption is another difficulty associated with spectroscopic measurements at high temperatures.

Shape of absorption lines

According to the discussion above, molecules may only absorb or emit light at certain frequencies. Observed absorption lines, however, are seen to absorb light over a range of frequencies. Absorption is maximum at the frequency predicted by the energy gap and decreases on either side of this maximum.

There are a number of processes that result in this broadening, and these processes perturb the line shape in different ways.
4.2. The relationship between line and gas properties

Natural broadening

Even if all other sources of line-broadening were eliminated, Heisenberg’s uncertainty principle would place a restriction on the width of absorption lines since

\[ \Delta E \Delta t > \frac{\hbar}{2}, \] \hspace{1cm} (4.10)

where \( \Delta E \) is the uncertainty in the energy level, \( \Delta t \) is the lifetime of the state and \( \hbar = h/2\pi \). In isolation, this is a weak effect but becomes important with the effect of collisions.

Pressure broadening

In a gas sample, molecules are continually colliding with each other and these collisions induce relaxation of the molecules back to the ground state, so that \( \Delta t \) is significantly smaller. Since more collisions occur at high pressure, the line is broadened by increasing the pressure. An analysis of this effect [25, e.g.] for a transition centred on \( \nu_0 \) and with a width at half-maximum of \( \gamma_l \) results in a Lorentzian line shape

\[ g(\nu) = \frac{1}{2\pi} \frac{\gamma_l}{(\nu - \nu_0)^2 + (\gamma_l/2)^2}, \] \hspace{1cm} (4.11)

as shown in figure 4.4.

For the present work, the Lorentz half-width, \( \gamma_l \), was typically used as a free-parameter when fitting absorption lines. Alternatively, for predicting spectra at expected environmental conditions, values of \( \gamma_l \) can be derived from parameters in the HITRAN database. This is limited to mixtures of air and water vapour and is given in the form

\[ \gamma_l = \gamma_{air}P_{air} + \gamma_{H_2O}P_{H_2O} \] \hspace{1cm} (4.12)

where \( \gamma_{air} \) and \( \gamma_{H_2O} \) are co-efficients for air and self-broadening respectively and \( P_{air} \) and \( P_{H_2O} \) are the respective partial pressures. Although \( \gamma_{air} \) and \( \gamma_{H_2O} \) are tabulated for all lines listed in HITRAN, it is only a subset these values which are based on measurement. This limits the accuracy of spectra calculated from HITRAN.

Doppler broadening

The translational motion of molecules in a gas sample also contribute to the absorption line shape. Although the molecules emit or absorb radiation at \( \nu_0 \) in their own reference frames, this frequency will be Doppler-shifted in the reference frame of a stationary observer. The resulting line shape perturbation is a direct result of the Maxwellian distribution of velocities in the sample and is given by

\[ g(\nu) = \frac{2}{\gamma_d} \sqrt{\frac{\log(2)}{\pi}} \exp \left[ -\frac{4 \log(2)}{\gamma_d} \frac{(\nu - \nu_0)^2}{2} \right]. \] \hspace{1cm} (4.13)
This function is shown along with a Lorentzian line shape in figure 4.4. Doppler broadening results in a line shape that has a smaller contribution from the wings of the transition when compared to pressure-broadening.

The Doppler half-width is dependent on temperature, \( T \), the molecular mass of the probed species, \( M \), and the transition centre frequency, \( \nu_0 \) so that

\[
\gamma_d = \frac{\nu_0}{c} \sqrt{\frac{2RT \log(2)}{M}}
\]

where we also have the speed of light, \( c \), and the universal gas constant, \( R \).

**Combined pressure and Doppler broadening**

If the effect of pressure broadening and Doppler broadening are treated as being uncorrelated, we can convolve equation (4.11) with (4.13) to arrive at an equation, known as the Voigt function,

\[
g(\nu) = A \frac{y}{\pi} \int_{-\infty}^{+\infty} \exp\left(-\frac{t^2}{2}\right) \frac{\nu - \nu_0}{(x-t)^2 + y^2} dt
\]

where

\[
A = \frac{\sqrt{\log(2)}}{\gamma_d \sqrt{\pi}}, \quad y = \frac{\log(2) \gamma_l}{\gamma_d} \quad \text{and} \quad x = \frac{\log(2) \nu - \nu_0}{\gamma_d}.
\]

This function can be calculated using Wells’ algorithm [127] with the addition here of the factor \( A \), which normalises the integral of the Voigt function to one.

When fitting the Voigt function to an observed line shape, generally both \( \gamma_d \) and \( \gamma_l \) are used as free parameters, except when temperature is known independently.

**More advanced line shapes**

Diode laser spectroscopy is an extremely effective means of gaining line shape information [63], so effective that experimental line shapes can be seen to depart from the Voigt function. A brief overview of the hierarchy of line shape models is provided by D’Eu et al. [26] in their comparison of experimental line shapes with models.

In 1953, Dicke [27] proposed that the confinement of a molecule, such as by other molecules in a gas, would result in the narrowing of the line width. Several models have since been developed which reflect this additional complexity.

Both the Galatry [39] and the Rautian and Sobel’man [96] profiles allow the phase of emitted radiation and the translational velocity to change at collisions. Galatry assumes that collisions are soft, so that many collisions are required to result in a large perturbation to the molecule’s motion. In contrast, Rautian and Sobel’man consider collisions to be hard, resulting in a molecule acquiring an essentially random motion after a single collision.
An alternative approach is to consider the dependence of transition collisional width and shift parameters on molecular speeds. This results in the speed-dependant Voigt profile [12], which produces asymmetric line profiles.

While the derivation of these different line models is arrived at from consideration of quite different physical situations, the different line models seem to perform similarly when fit to experimental data [26, 63]. The numerical value and meaning of line shape parameters produced by the fit differ between models, which can make it difficult to base conclusions on these values. Where lines are being fit for the purpose of finding the line strength, however, this poses no problem. Fitting a Voigt function to a line shape when a more sophisticated model is required results in characteristically shaped residuals, published in the literature [26, 63, 70]. These are shown in figure 4.5, which has been generated by fitting a Voigt profile to a theoretical line shape generated with a Galatry model. In this example the Doppler width has been fixed to its known value, but allowing the Doppler width to vary results in much smaller residuals as the fitting procedure reduces the Doppler width to better fit the shape of the Galatry profile.

Galatry profiles are the only profiles computed for this work that take Dicke narrowing into account and were calculated using the method reported by Varghese and Hanson [122].

4.3 Spectral model of water vapour

In conjunction with an appropriate spectroscopic database, the theory presented in this chapter is enough to build a spectral model of water vapour. For this work a spectral model known as GENSPECT [94] was used. This is implemented as a MATLAB toolbox and was freely available in mid 2001, however it is not clear if it is still available. Fortunately other models can be obtained, such as RFM [30], which perform a similar function.

These models, in principle, operate in the following manner:
• Line parameters are loaded from a database such as HITRAN [98];

• Equation (4.6) is used to scale the line strength from the tabulated reference strength to the desired temperature;

• A correction is applied to the line centre location based on pressure, as given by Rothman et al. [97];

• Pressure and Doppler broadening parameters are calculated according to equations (4.12) and (4.14) respectively;

• Each spectral line is evaluated individually using a specialised algorithm, such as that given by Wells [127], using the line parameters above. This step is where most of the processing time is taken up, so there are various strategies used to speed evaluation of the line shape while retaining a specified error tolerance, for example the interpolation scheme used in GENSPECT [94]; and

• Contributions from the individual lines are added and the transmission is calculated based on the line strength, absorber density and path length.

Generally the various models have more capabilities than this and may include the ability to simulate absorption across atmospheric paths, calculate absorbance for many species besides H$_2$O or include CO$_2$ line-mixing effects, among other features. For this work, however, the main requirement was simply to obtain a first-estimate of the characteristics of the water vapour spectrum both over a large spectral range, as shown in figure 4.6, and over a small spectral range where measurements would be made but at different temperatures, as shown in figure 4.7.

Since the method of predicting the spectrum relies on a database of line parameters, inaccuracies in the underlying database result in an inaccurate prediction. As a consequence of this ability to predict the spectrum, the theory allows for the measurement of temperature and water vapour concentration provided that the absorbance of two spectral lines can be measured.
4.3. Spectral model of water vapour

Figure 4.6: Water vapour spectrum between 1 and 2\( \mu \)m. Transitions in the \((1, 0, 1) - (0, 0, 0)\) vibrational band are shown in black.

Figure 4.7: Water vapour absorption at 500, 1000 and 1500 K simulated from HITEMP for a total pressure of 20 kPa and a mixture of 10% by volume of water vapour in air.
4. Absorption spectroscopy theory