Determination of acetylene's moments of inertia in its ground and first excited vibrational states

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Abstract

The **MATLAB** program, **H2OCalibrate_C2H2Analyse.m**, which provides results for this report, given as an appendix, has the purpose of determining the moment of inertia of acetylene (**C2H2**) from differential spectroscopic data. A calibration is made by using spectral data (intensity of against channel number) of water (**H2O**) and known wavenumbers at the peaks. An accurate (quadratic) model of the variation of C2H2 peaks with m was compared with theoretical predictions, giving the following moments of inertia:

$$I_0 = 2.3461 \times 10^{-46} \pm 1.0490 \times 10^{-48} \quad ,$$

$$I_1 = 2.4031 \times 10^{-46} \pm 1.0974 \times 10^{-48} \quad , \quad \&$$

$$\Delta I = I_1 - I_0 = 5.7070 \times 10^{-48} \pm 2.0461 \times 10^{-49} ,$$

where I_0 is the moment of inertia of C2H2 in its ground state, and I_1 is its moment of inertia of it in its first excited vibrational state. Using these moments of inertia with the classical moment of inertia formula, an approximation for the C-C bond length can was found to be around 1 angstrom.

Introduction

The data used in this program is differential spectrum data, which looks like the curve described by the red dots in figure 1. The data for both H_2O and C_2H_2 contains peaks which look like this. The peak of interested is the peak described by the blue dots in figure 1, and as can be seen, its position is the mean position of the red peaks.
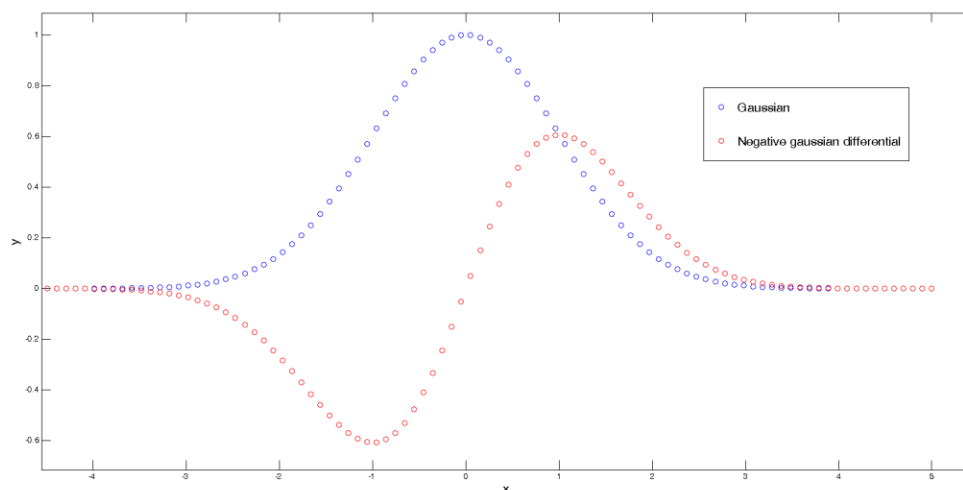

Figure 1: A comparison of the Gaussian curve and its differential is presented. To find the channel number of where the actual peak in data is, the mean channel numbers of the two peaks on the differential curve can be used.

By default, **MATLAB** interprets the 1801 points of data as y values, and assigns their index to an x value, allowing them to be graphed and otherwise manipulated. Four wavenumbers were provided for the four "actual" peaks in the H_2O spectrum, so these peaks were isolated and the gradient of a graph of channel number against wavenumber was taken, so that the calibration (and the error in this) of the spectrometer was known. Chi-squared, residual, and expected-error analyses suggest that this value for calibration is acceptable as expected values produced from best fit parameters match the real data.

To see whether the moments of inertia of the ground state and the first excited state of C_2H_2 are the same, equation 3 can be used. If the channel numbers of the C_2H_2 peaks scale linearly with m, then these moments of inertia are the same – and if the relationship is quadratic, they are different. Chi-squared analysis shows which of these fits is more accurate, thus how data should be interpreted.

The resolution and range of the spectrometer will be considered in the discussion later on, as well as consideration of the breadth of the peaks in the data and its attribution to Doppler broadening.

Theory

One important consideration in getting to equation 3 is electric dipole transitions. The wavefunction describing the atomic state during a transition from an initial state to a final state can be written as a combination of initial and final wavefunctions.

The overall parity (a form of symmetry) of the integral of these wavefunctions multiplied together and by the vector distance must be even to produce a non-zero integral over all space. It is known that the vector distance has odd parity, thus one of the initial and final states must have odd parity, and the other even parity. This implies the quantum number "l" changes by an odd integer in radiative transitions - this is the second selection rule. [1]

By considering a quantum simple harmonic oscillator and the rotational angular momentum of a pair of atoms (which comprise a molecule, in this case the carbon atoms in C2H2), the energy of this system can be approximated as

$$E_{n,l} = hf\left(n + \frac{1}{2}\right) + \frac{\hbar^2 l(l+1)}{2I} \qquad , \qquad\qquad 1$$

where f is the frequency of vibration, n and l are quantum numbers (for vibrational and rotational energies respectively in this case), $\hbar$ is a constant, and I is the moment of inertia, equivalent to

$$I = \sum_i m_i r_i^2 = 2M\left(\frac{L}{2}\right)^2 \qquad , \qquad\qquad 2$$

where M is the sum of the mass of hydrogen and carbon, L is the carbon-carbon bond length, and the factor of 2 at the front is due to symmetry. [2]

Using the second selection rule and equation 1, the energy difference between neighbouring states can be written (after grouping like terms) as

$$\Delta E_m = hf + \frac{\hbar^2}{2}\left(\frac{1}{I_1} + \frac{1}{I_0}\right)m + \frac{\hbar^2}{2}\left(\frac{1}{I_1} - \frac{1}{I_0}\right)m^2 \qquad . \qquad\qquad 3$$

Preparing data & calibration

Before performing calibration, the spectroscopic data had to be prepared. Firstly, both sets of data were graphed, and the pairs of peaks (4 pairs for H2O, 5 for C2H2) were isolated by creating subsets of data. A channel error of 0.5 was assigned to both sets of data, which is then used with itself in quadrature to find the channel error on the mean channel, where the actual peak is. To find the mean channel, the maximum and minimum intensities in the subsets were found, and the mean was taken of their indexes. These were then added to the number of indexes between one and where that subset of data starts.
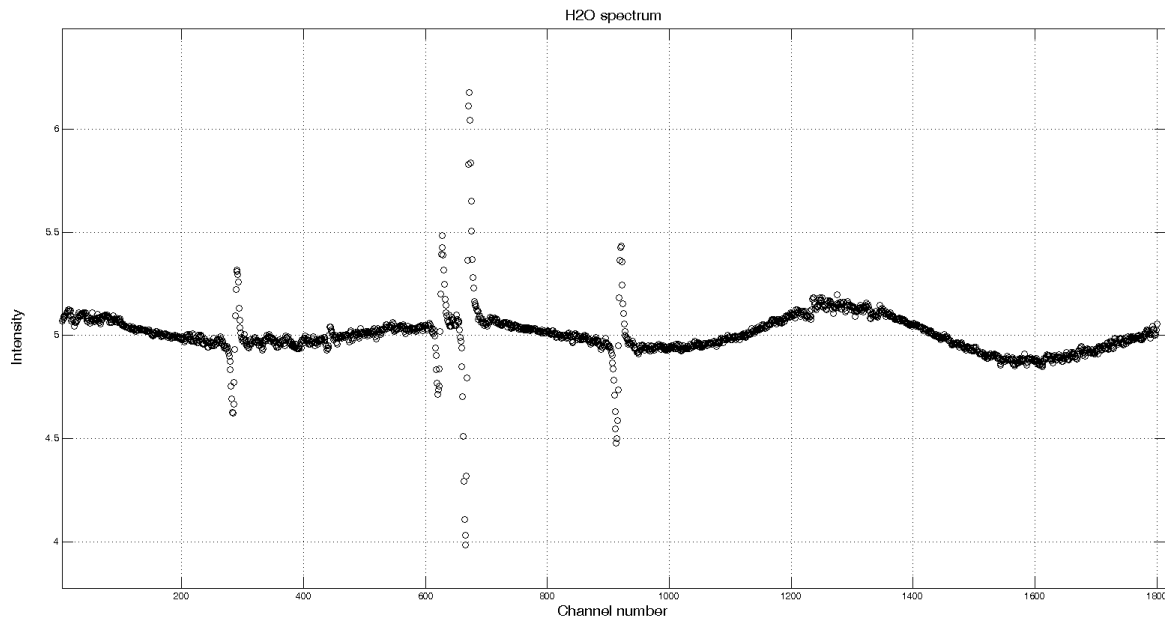

Figure 2: As can be seen, there are easily four identifiable peaks in the H2O spectrum. The mean channel number of the minimum and maximum peaks is required in order to perform calibration.
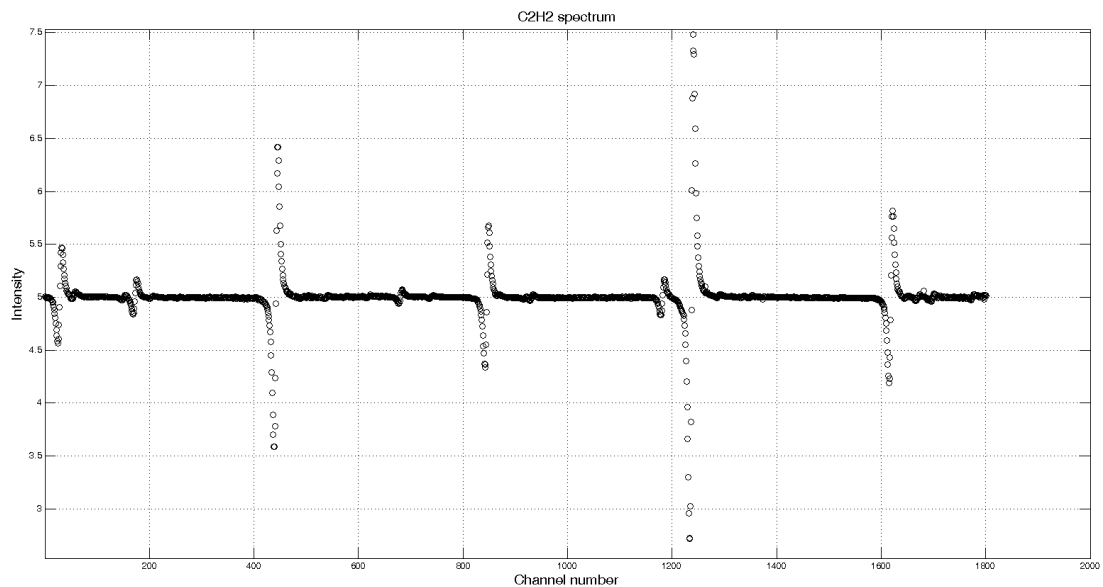

Figure 3: The C2H2 spectrum is similar to that for H2O, and the mean channel numbers of the maximum and minimum peaks are extracted in exactly the same way.

Using the given wavenumbers of these four H2O peaks (12683.782, 12685.540, 12685.769, 12687.066 cm^{-1}), and the four isolated channel numbers, the figure 4 was produced.
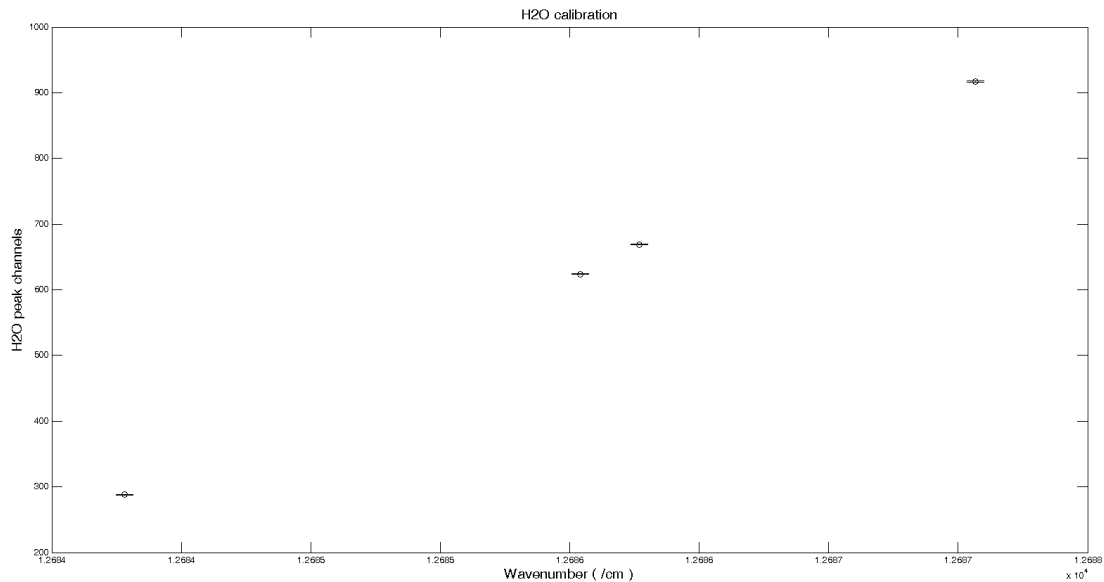
Figure 4: The gradient of this graph will be channels per wavenumber, and the reciprocal of this (wavenumber per channel) will be used later on. A conversion factor of 100 will be used to shift units into metres, giving the conversion factor F.

In **MATLAB**, the "*polyfit*" command can create two data structures − one contains the best fit parameters (e.g. gradient and y-intercept for a linear fit), and the other contains data which can be used to find errors. The "*polyval*" command can create points based off these parameters at some given points. Figure 5 shows a residual plot − the y values are the fitted *polyval* channels minus the actual channels.

Using the assigned channel error (after being manipulated by quadrature) and data from the *polyfit* error structure, the value of Chi-squared for this fit was found to be 1.34. The error structure also suggested that the expected error would be around 0.58, thus the values from the *polyfit* model match the data well, and the gradient obtained for calibration is acceptable.
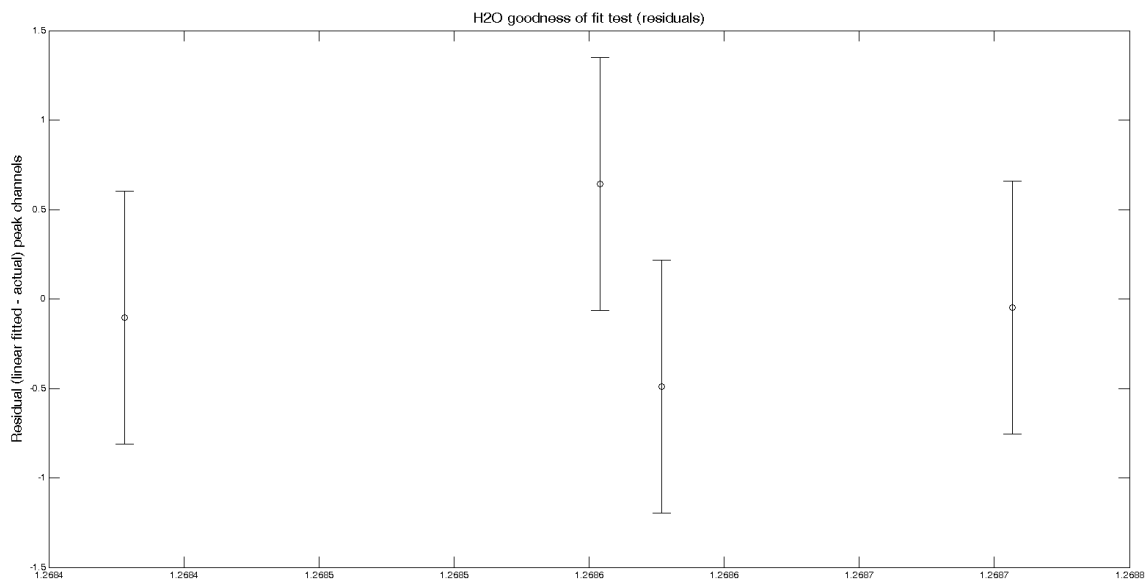

Figure 5: This graph suggests the linear fit is good - residuals are small, and they're all relatively close to each other. The Chi-squared value verifies this goodness of fit.

The key item obtained from this analysis is the conversion factor, F. This was mentioned in figure 4, and it converts a channel number into a wavenumber.

Analysing C2H2 data

Using the same *polyfit/polyval* steps as were just described for analysing the H2O data, whether the C2H2 data scales linearly or quadratically with the m was be determined. Whichever fit produces an acceptable value of Chi-squared was used.
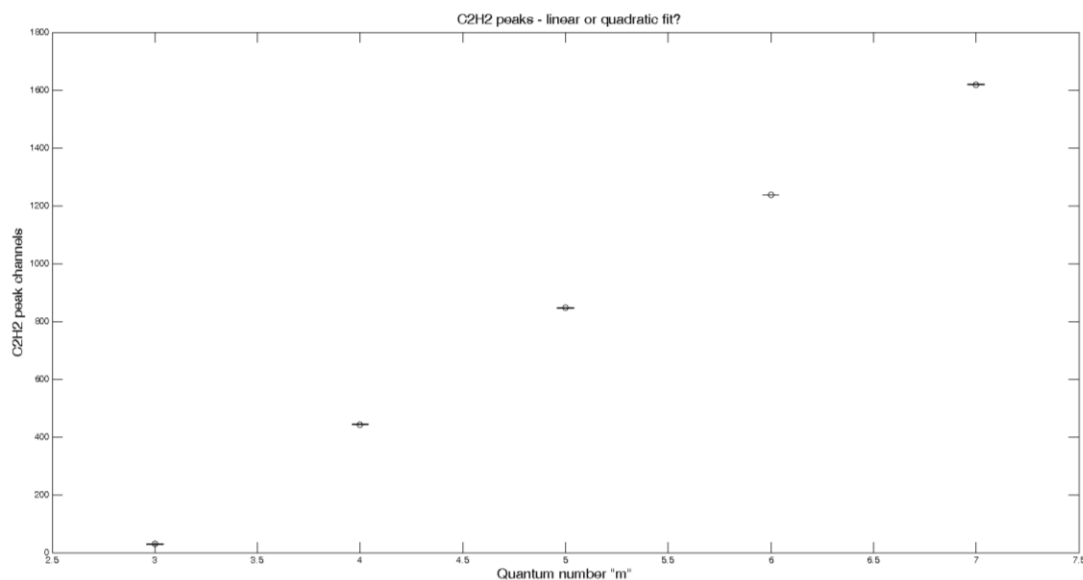

Figure 6: These regularly spaced peaks look like a linear fit would be good, but a thorough error analysis is necessary to see if a quadratic fit is significantly better.

The Chi-squared value for the linear fit, residuals shown in figure 7, was 826.4. The Chi-squared value for the quadratic fit, residuals shown in figure 8, was 1.26. This, and the residual plots, suggest a quadratic fit is a good fit (and a linear fit isn't acceptable), and thus a quadratic fit will represent the data. The quadratic fit is good enough that a higher order fit isn't necessary.
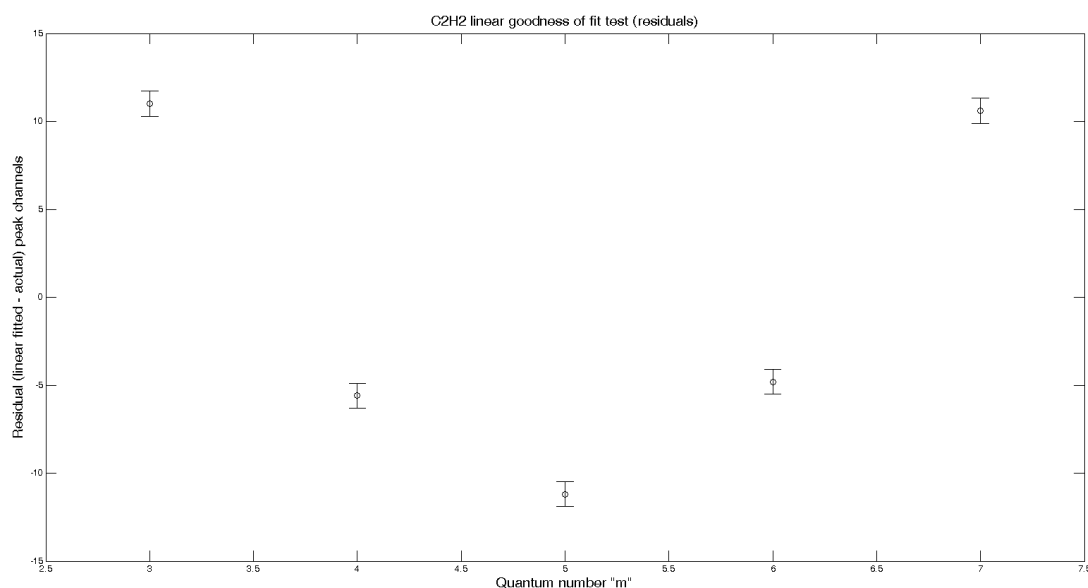

Figure 7: The residuals for the linear fit are quite large, especially when considering the relative size of the error.
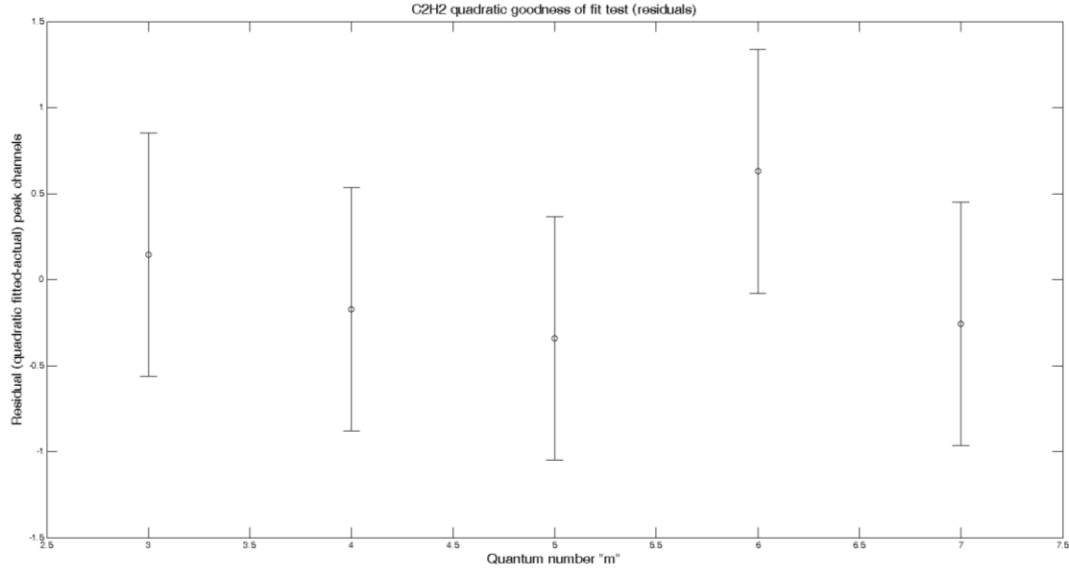
Figure 8: This residual plot suggests the quadratic fit for the C2H2 data is much more appropriate than a linear fit.

Now that an accurate model of the data is obtained, comparison with equation 3 can be made. The quadratic fit implies two different moments of inertia, which will be calculated. Our best-fit parameters, when multiplied by the relevant quantity of m, give a channel number. Multiplying these terms by the conversion factor obtained through the H2O calibration, F, gives a wavenumber. Multiplying these terms by the speed of light and the Planck constant gives an energy:

$$n_{ch}.F.hc = F.hc.A + F.hc.B.m + F.hc.C.m^2 \quad . \qquad 4$$

By equating coefficients of equation 4 and equation 3 and rearranging, the moments of inertia can be written as

$$I_0 = \frac{\hbar^2}{FhcD_0} \quad \& \qquad \qquad 5$$

$$I_1 = \frac{\hbar^2}{FhcD_1} \quad , \qquad \qquad 6$$

where $D_0 = B - C$ and $D_1 = B + C$. The errors on B and C were extracted from the error part of the *polyfit* array for the quadratic fit and the errors on D_0 and D_1 were found by quadrature, Multiplication is used to find I_0 and I_1, so fractional error analysis is used to find the errors in the moments of inertia.

With more rearrangement, and making the approximation that C^2 is negligible when added to B^2, an expression for the difference in moment of inertia is arrived at, and its error can be found with by fractional errors:

$$\Delta I = -\frac{\hbar^2}{Fhc}\frac{2C}{B^2} \quad . \qquad \qquad 7$$

Using equation 2, the C-C distance was found to be 1.04 angstroms for the ground state, and 1.06 angstroms for the excited state – these are typical interatomic atomic distances, thus the moments of inertia appear acceptable.

Discussion

The spectrometer clearly has a limit on the range of channels. Multiplying this by the conversion factor, this equates to a range (in wavenumbers) of about 940 per metre. This equates to a range of about one million nanometres. Dividing through by the number of channels, it is found that the spectrometer has a resolution of about 590nm per channel. Obviously more channels would have given more accurate data, however analyses suggest that data was able to be modelled with good accuracy.

If a molecule has relatively abundant isotopes, then there will be clear splitting of peaks due to isotopes causing different moments of inertia. These were not seen in the data, probably because carbon is mostly carbon-12, and hydrogen is mostly protium – different isotopes may have been in the sample, but their intensities may have been too small to notice them.

The actual peak does not have finite width due to that effects, such as Doppler broadening and natural line width. Natural line width is due to the uncertainty in energy of states involved in radiative transitions, but it is less significant in atomic spectroscopy than nuclear spectroscopy, where transitions can have short times associated with them and thus high uncertainties in energy.

Doppler broadening is due to the thermal motion of the particles moving towards or away from the detector – a Doppler shift gives a change in wavelength. The temperature of particles has a Boltzmann distribution, and particles moving at different speeds will have different Doppler shifts. Across all the particles, this produces Doppler broadening. Unfortunately a value wasn't obtained for an estimate on how many channels the Doppler effect broadens the peaks by, however it should be less than the width of the peaks as there are other broadening effects as well. [3]

Conclusion

This whole process could be applied to any other spectroscopic sample which emits or absorbs radiation in the range of a spectrometer. As is the case here, both sets of data must of course be obtained from the same spectrometer, and wavenumbers must be known for one set of data so calibration can be performed. To confirm the moments of inertia obtain were acceptable, the C-C distance was estimated with them – however, in principle, if a substance were completely unknown the interatomic distance may be determined by a mix of absorption spectroscopy and mass spectrometry.

References

[1] Eisberg, R., Resnick, R. *Quantum physics of atoms, molecules, solids, nuclei, and particles, 2nd Edition*, United States of America, Hamilton Printing Company, 1985

[2] - Freedman, R., Young, H. *University Physics*, *13th Edition*, United States of America, Pearson Education Limited, 2013

[3] Haken, H., Wolf, H.C. *The Physics of Atoms and Quanta*, 5th Ed, Springer-Verlag, 2000