Water Line Parameters from Refitted Spectra constrained by empirical upper state levels: study of the 9500 – 14500 cm^{-1} region

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July 31, 2007

Abstract

A fitting technique is proposed which gives more reliable spectral line parameters for blended and very weak lines. The technique uses common upper state energies to fix frequencies in cases where these are poorly determined. Room temperature Fourier Transform absorption spectra of pure water vapor due to Schermaul *et al* (J. Mol. Spectrosc., 208, 32 (2001) and 211, 169 (2002)) recorded at several pathlengths are refitted. Parameters are obtained for over 10700 transitions of $\mathrm{H_2}^{16}\mathrm{O}$ covering the frequency region 9500 – 14500 cm^{-1}. Only 73 of the lines remain unassigned. Comparisons with previous studies on water vapor absorption in this region suggests that the new parameters give a more consistent representation of the underlying spectrum.

1 Introduction

Water vapour spectra have been studied both theoretically and experimentally for decades. Knowledge of these spectra is vital for atmospheric and astronomical studies, and much else. However the spectrum of water is difficult to characterise. It has a large dynamic range and, in the near infrared and red region considered here, contains large numbers of blended lines. Its use in long-path length studies, such as satellite observations of the earth's atmosphere, mean that even weak features in laboratory spectra are important for practical applications.

In this work we re-examine water vapour spectral line parameters in the region 9500 – 14500 cm^{-1}. This part of the spectrum could be considered well studied after works of Brown *et al* [1], Mérienne *et al* [2], Coheur *et al* [3] and Schermaul *et al* [4, 5, 6, 7]. Figure 1 compares the line frequencies reported by Brown *et al* [1] and Mérienne *et al* [2]. Apart from the small systematic shifts, which are different for strong and weak lines, the comparison shows that for a large number of line positions there is significant disagreement between the two studies. This disagreement reflects the statistical fitting errors for these particular lines. The two main causes of these errors are: noise, which strongly affects the parameters of weak lines, and overlapping or blended lines which affects strong lines as well as weak ones.

Spectral lines correspond to quantum mechanical transitions between two stationary states of the molecule. In the case of negligible pressure shifts the transition frequency (in cm^{-1}) ν_{fi} is defined by the relation:

$$\nu_{fi} = E_f - E_i, \tag{1}$$

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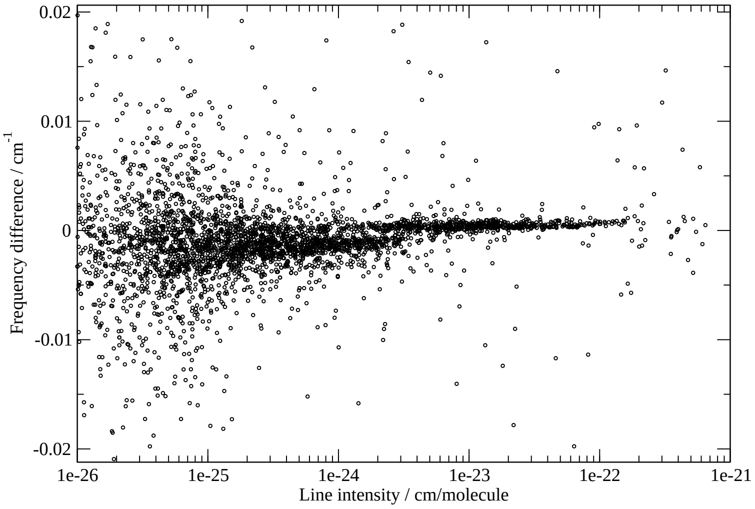

Figure 1: Comparison of line positions from works of Brown *et al* [1] and Mérienne *et al* [2] in the region between 9500 and 11500 cm^{-1}.

Table 1: Summary of the spectra and experimental conditions: p is pressure of pure water vapor, T temperature and pathlength L.

#	Range (cm^{-1})	p (hPa)	T (K)	L (m)	$(2L)^{-1}$ (cm^{-1})
1	8500–15000	9.495	294.9	4.938	0.03
2	8500–15000	10.017	294.4	32.75	0.03
3	8500–15000	10.008	295.7	128.75	0.03
4	8500–15000	10.094	295.6	512.75	0.03
5	9200–12800	22.93	295.7	800.8	0.011
6	11800–14500	21.15	296.0	800.8	0.013

where E_f and E_i are the energies of the upper and lower state respectively. Typically, a rotation-vibration absorption spectrum contains several transitions to a particular upper state. If the lower state energies are known (eg [8, 9]) and the frequency of one of the transitions to an upper state is determined with good accuracy, then the energy calculated from Eq. (1) can be used to predict the centres of the other transitions to this upper state. When the predicted line centres correspond to lines which are very weak or blended, then the calculated value may be more accurate than that obtained directly by fitting. As we show, use of this procedure results in better determined fits and more consistent sets of line parameters. It should be noted that the method requires assignment of the spectrum before the final fit can be performed. Related methods have been used for systems where it is easy to construct an effective Hamiltonian of the system [10], which is not the case for water.

2 Method and data analysis

In this work we use the energy constraint outlined above to derive line positions, intensities and self-broadening coefficient of water vapour in the region 9500 – 14500 cm^{-1}. The main assumption made is that the frequency error for blended and weak lines in a traditional, unconstrained approach is bigger than pressure-induced line shifts. Only in this case does fixing line positions according to Eq. (1) improve the retrieved line parameters.

Experimental and theoretical studies of the self-induced line shifts (see e.g. Zou and Varanasi [11] and Antony *et al* [12]) suggest that they are unlikely to exceed 0.1 cm^{-1} atm^{-1} which gives a maximum shift of 0.001 cm^{-1} shift at 10 hPa. In the spectra considered here, only strong isolated lines can have fitting uncertainties smaller than 0.001 cm^{-1}; traditional fit of blended and very weak lines in these spectra give much bigger errors.

In this work we re-fit six room temperature pure water vapour absorption spectra recorded and published earlier. The first four spectra are number 1, 3, 6, and 9 measurements from Table 2 of Schermaul *et al* (2001) [4]. These spectra cover the region of 8500 – 15000 cm^{-1} and were recorded with path lengths from 5 up to 512 m. They are be referred to as short path spectra. The two other spectra were taken from Schermaul *et al* (2002) [5] and have numbers 2 and 3 in Table 1 of that work. These spectra, referred to as long path, were recorded with an 800 m path. The summary of the experimental conditions of the used spectra is given in Table 1.

The short path spectra were not originally frequency calibrated by Schermaul and co-authors as they did not use these spectra for line parameter retrievals. We calibrated these spectra using the $H_2{}^{16}O$ data from the HITRAN 2004 database [13]. The water vapour data in HITRAN 2004 in the 9500 – 14500 cm^{-1} region is taken from the work of Brown *et al* [1] below 11500 cm^{-1}, and of Mérienne *et al* [2] and Coheur *et al* [3] above 11500 cm^{-1}. As can be seen from Figure 1 there is a systematic disagreement between the two datasets, so a small systematic error can be also expected in the data we produce. The long-path spectra, 5 and 6 of Table 1, were already calibrated and they are in 0.0003 cm^{-1} or better agreement with Brown *et al* [1].

Schermaul *et al* fitted their spectra using a generalised Voigt profile i.e. one in which contains a damping parameter which effectively allows the Gaussian profile to vary from its theoretical value determined by the ambient temperature. This parametrisation makes it difficult to compare with other spectra fitted to standard Voigt profiles. Indeed a number of published comparisons with both Schermaul *et al*'s pure water vapor [4, 5] and water-air [6, 7] have simply ignored the damping parameter. Such a comparison is not really valid.

Here we employ standard Voigt profiles with the Gaussian contribution fixed to its theoretical value to simulate the line shape. The aim was to find central frequencies, intensities and self-broadening coefficients of all lines in the region which minimize the residuals in all six spectra and aims to constrain the frequencies to satisfy Eq. (1). Line parameters and assignments from Tolchenov *et al* [14] were used as the initial data. Energies for the lower states were taken from Toth [8]. Although the intensities were treated as independent for every line, in some cases of blended and very weak lines they were constrained not to deviate significantly from calculated values. For this the BT2 (Barber *et al* [15]) variational line list was used. The instrumental functions were taken as a convolution of a sinc and a boxcar function. Its finite aperture contribution was adjusted to improve the fit. All intensities in the text, figures and tables are given in cm/molecule for the temperature of 296 K.

The analysis started with recalculating the line centres using Eq. (1) with upper state energies averaged over the transitions from the initial line list. Then the parameters were fitted to the experimental spectra. Beginning with the shortest paths, the spectra were analysed one at a time. The line list was scanned from lower to higher frequencies to find a line with the maximum absorbance between 0.1 and 1 in the current spectrum. When such a line was found it was checked to see if its parameters needed adjusting. Before fitting the line (the current line) its upper level was determined and all other transitions to that level were also found. The lines of this group were treated differently depending on whether or not it was the first time its upper level was encountered. If it was the first time, then the strongest, most isolated “best” line was selected. The selected line was fitted using a least-squares fitting procedure. Its new line centre was then used to recalculate the positions of all other lines in the group. The intensity and self-broadening coefficient of the current line were then adjusted. If the resulting fit was not satisfactory the frequency was also fitted.

If the upper level had already been dealt with before using the above procedure, the current line was fitted with its frequency frozen. If the residuals of the fit showed an asymmetric feature the line position could also be fitted. Sometimes the shift of the line was caused by a close weaker line whose parameters were not in the initial line list. In such a case a line could be added to the experimental line list and assigned using the BT2 line list. The upper level of the new line was then investigated. If it was known from a previous analysis the new line's frequency was calculated accordingly and an attempt to fit only the intensities of the overlapping lines was made. If it was unsuccessful the frequency of one of the lines (usually the weaker one) was varied. Blends of three or more component lines often had to be considered.

It was not possible to resolve all blends using this technique. If a feature was a sum of two single lines, i.e. the upper state is determined by only one transition, they were subjected to a traditional unconstrained fit. About 80 blends were fitted as if they had only one component but given a double assignment.

The long and short path length spectra showed inconsistent pressure broadening. The long-path length spectra give systematically larger self-broadening coefficients. An attempt was made to bring them into agreement by adjusting the instrumental functions but it did not give a satisfactory result. The coefficients obtained from the long path length spectra were chosen for the final line list as these spectra have wider lines due to higher water vapour pressure and they also have higher resolution compared to the short path length spectra.

Self-broadening coefficients of the individual lines were either set free or fixed depending on stability of the fit. For the weakest and blended lines these widths were usually held fixed in the fit. In the line list given in the electronic archive, the fixed broadening parameters can be identified as having only one significant digit.

Table 2: Transitions to the level (201) 3_{30}.

		Brown *et al* [1]			This work			
#	Lower level	ν	I	E	ν	I	E	Comments
1	(000) 4_{31}	10490.9286	3.0e-23	10874.7711	10490.9288	3.1e-23	10874.7714	isolated
2	(000) 3_{31}	10589.5679	9.1e-23	10874.7873	10589.5520	1.5e-22	10874.7714	blended
3	(000) 4_{13}	10599.2813	4.2e-26	10874.7783	10599.2743	1.5e-26	10874.7714	weak
4	(000) 3_{13}	10732.4946	1.3e-25	10874.7731	10732.4929	1.3e-25	10874.7714	close to a strong line
5	(000) 2_{11}	10779.5960	1.3e-24	10874.7719	10779.5958	1.4e-24	10874.7718	isolated

ν is the line centre in cm^{-1}, I is the line intensity in cm/molecule, E is the upper state energy in cm^{-1} derived from the transition using Eq.1.

3 Results

As result a list of parameters was constructed for 12031 transitions of which 10709 lines belong to the $H_2{}^{16}O$ water isotopologue and only 73 lines are unassigned. The initial line list contained 10908 lines including 772 unassigned. The majority of the original unassigned lines were either too weak to be seen under the noise or not confirmed as genuine lines in our analysis.

The parameters reproduce unsaturated lines (with the above remarks concerning the self-broadening coefficients) so that the residuals are below the noise level. The wings of saturated lines are simulated with lower accuracy as the Voigt profile is not an exact line shape. This is illustrated in Figure 2. It shows three experimental spectra (3, 4 and 5 of Table 1) in the same spectral region. The position, intensity and self-broadening coefficient of the strong central line were obtained from fitting to spectrum 3 (Figure 2 upper). As the line saturates (Figure 2 lower) the calculated profile strongly deviates from the experimental one. The weaker lines fitted to spectrum 5 (Figure 2 lower) show small disagreement compared to spectrum 4 (Figure 2 middle).

Figure 3 illustrates how Eq. (1) is satisfied for both the initial line list (left) and the lines fitted with the technique used in this work (right). The new fit gives a significantly narrower distribution which means that many more lines comply with Eq. (1). It should be noted that the majority of the non-zero differences in Figure 3 (right) result from fitting good, isolated lines. Thus, they must reflect the actual distribution of the pressure shifts of the lines. The wider distribution of Figure 3 (left) can be only due to fitting errors of weak and blended lines. This confirms our initial assumption.

To illustrate how the method helps to resolve blends let us consider two transitions (201) 0_{00} - (000) 1_{01} and (201) 3_{30} - (000) 3_{31} which form a blend with the separation between the centres of 0.01164 cm^{-1} (in this study). These are strong transitions for this spectral region with intensities greater than 10^{-22} cm/molecule. The parameters of the two lines are strongly correlated with the present experimental conditions so that a direct multi-line fit would give big fitting errors. This explains the big differences between the present work and Brown *et al* (see Figure 4). The first line is the only transition observed to (201) 0_{00} level, so the upper state energy of this level can be only determined from that line.

To illustrate our procedure let us consider the level (201) 3_{30} in detail. There are five transitions to (201) 3_{30}. They are detailed in Table 2. Lines 1 and 5 are well isolated and were fitted independently in this work. Their central frequencies are in a good agreement with those of Brown *et al* [1]. The positions of lines 2, 3, and 4 are more problematic; for example 4 is 0.24 cm^{-1} from the 10732.2530 cm^{-1} (201) 7_{35} - (000) 6_{34} transition which is more than 500 times stronger than it so even an apparantly well separated line is actually influenced

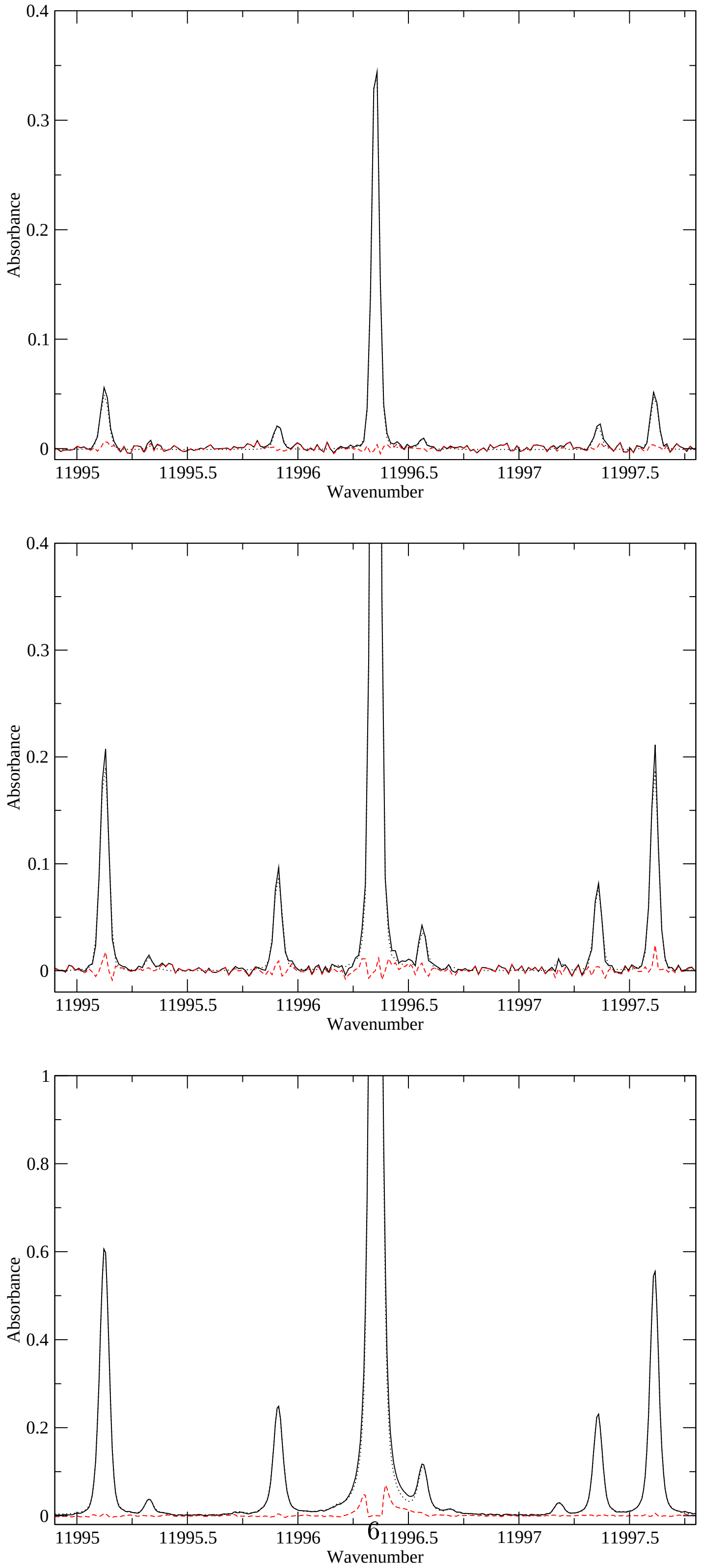

Figure 2: Portions of three experimental spectra with path lengths 128.75 m (upper), 512.75 m (middle), and 800.8 m (lower). The solid line is the experiment, the dotted line is the calculation and the dashed line is the residual.

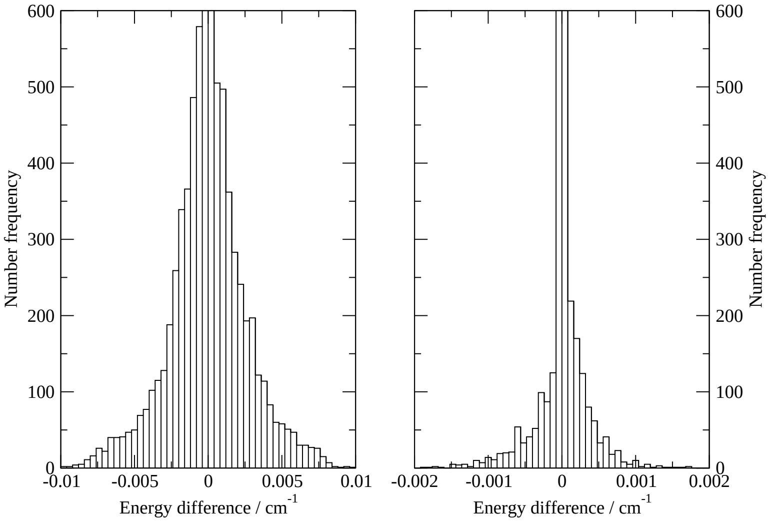

Figure 3: Energy difference distributions for the initial (left) and the final (right) line lists. The differences are between the mean energy value for a particular upper state and the value derived from an individual transition. The same transitions set was used for both plots.

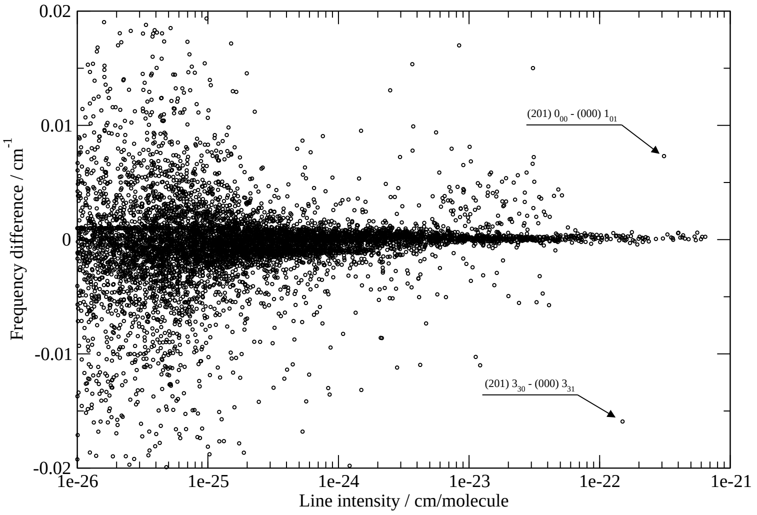

Figure 4: Comparison of the line positions from this work with those from the HITRAN 2004 database [13] as function of line intensity at room temperature.

by the wings of this transition. In our fits the upper state energy was obtained from transition 1. Assuming that the pressure induced shifts do not exceed 0.001 - 0.002 cm^{-1}, this must give more accurate frequencies than the direct fit. Fixing the frequency of the transition (201) 3_{30} - (000) 3_{31} (line 2 of Table 2) makes the parameters of the (201) 0_{00} - (000) 1_{01} line less correlated and more accurate.

Figures 5-7 compare line positions and line intensities from this work and those from HITRAN-2004 database in three regions separately to illustrate the different behavior in the three regions. These, and other comparisons with published spectra made here, all relied on line positions and intensities to make comparisons since not all spectral assignments agree. The best agreement is in the region below 11500 cm^{-1}. There is a very small shift in frequency and our intensities of the strong lines are systematically higher by about 3 %. In the two other regions agreement between the parameters of the stronger line is not so good.

In the region 11300 – 12850 cm^{-1} our intensities can be compared with those obtained by ICLAS technique by Mazzotti *et al* [16] who studied very weak water transitions. Figure 8 plots ratios of the intensities from the two studies against the line intensities of this work. The agreement seems to be reasonable taking into account that lines weaker than 10^{-26} cm/molecule are just above the noise level in our spectra. The exceptions are 4 strongest lines with intensities greater than 5×10^{-26} cm/molecule. These lines are higher than the intensity cut-off used in [16] and could be saturated there.

Our parameters also systematically agree with the original analyses of the long-path length spectra in [5], [17], and [18].

The line centres found in this work were used to calculate 3159 energies belonging to 44 vibrational bands. The full list of line parameters and energy levels can be obtained from the linelist and energy level files which are given in the electronic material associated with this article.

4 Conclusion

We have developed a new fitting technique which uses line assignments to improve quality of retrieved parameters of blended and weak lines. The method gives good results when the errors in the positions of problematic lines are greater than pressure induced shifts. The method was used to reanalyse the water vapour spectra recorded by Schermaul *et al* (2001) and Schermaul *et al* (2002) in the 9500 – 14500 cm^{-1} spectral region. As a result a list of $H_2{}^{16}O$ line parameters was produced containing more than 12000 transitions. These parameters will form part of the input of the IUPAC task group constructing a database of water transitions from experiment and theory. They should also provide a good starting point for the analysis of line profiles which, of course, requires further spectra recorded as a function of broadening gas, gas pressure and even temperature.

Acknowlegments

We thank Linda Brown for helpful comments on the manuscript. This work was supported by the UK Natural Environmental Research Council. The study was performed as part of IUPAC task group 2004-035-1-100 on A database of water transitions from experiment and theory.

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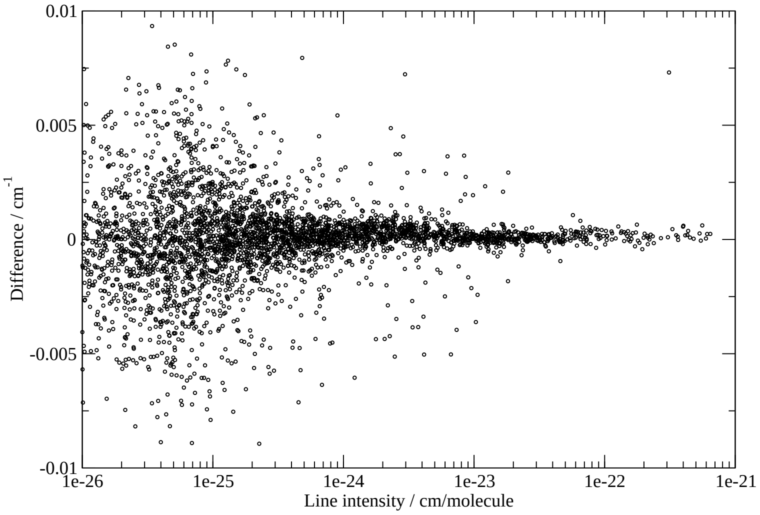


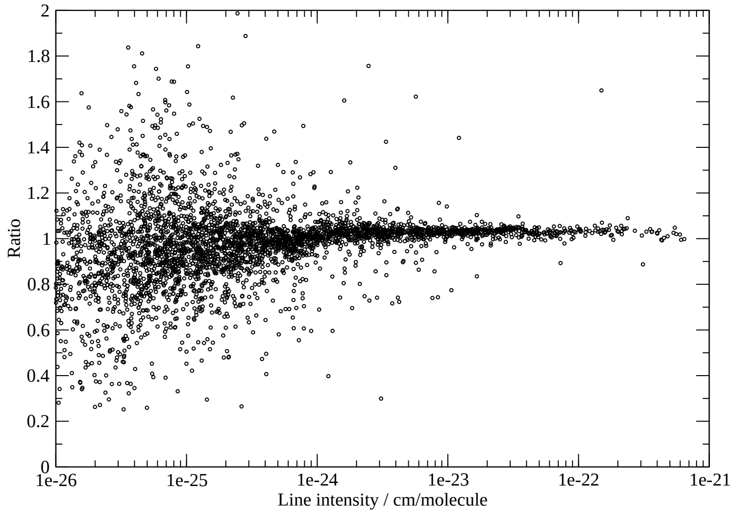
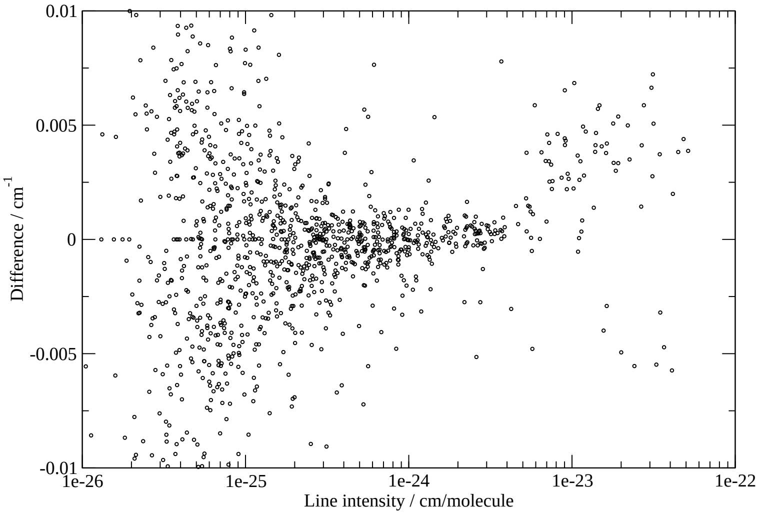


Figure 5: Comparison of the line positions (upper) and line intensities (lower) from this work with those from the HITRAN 2004 database [13] as function of line intensity at room temperature in the range 9500 – 11500 cm^{-1}.



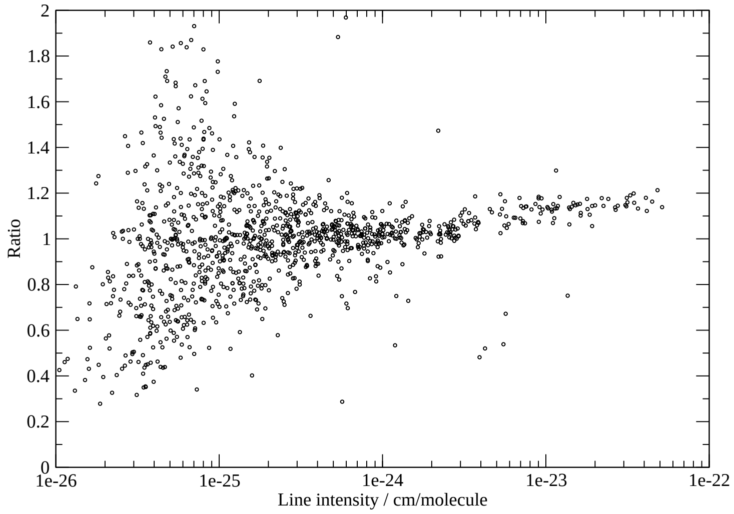


Figure 6: Comparison of the line positions (upper) and line intensities (lower) from this work with those from the HITRAN 2004 database as function of line intensity at room temperature in the range 11500 – 13000 cm^{-1}.

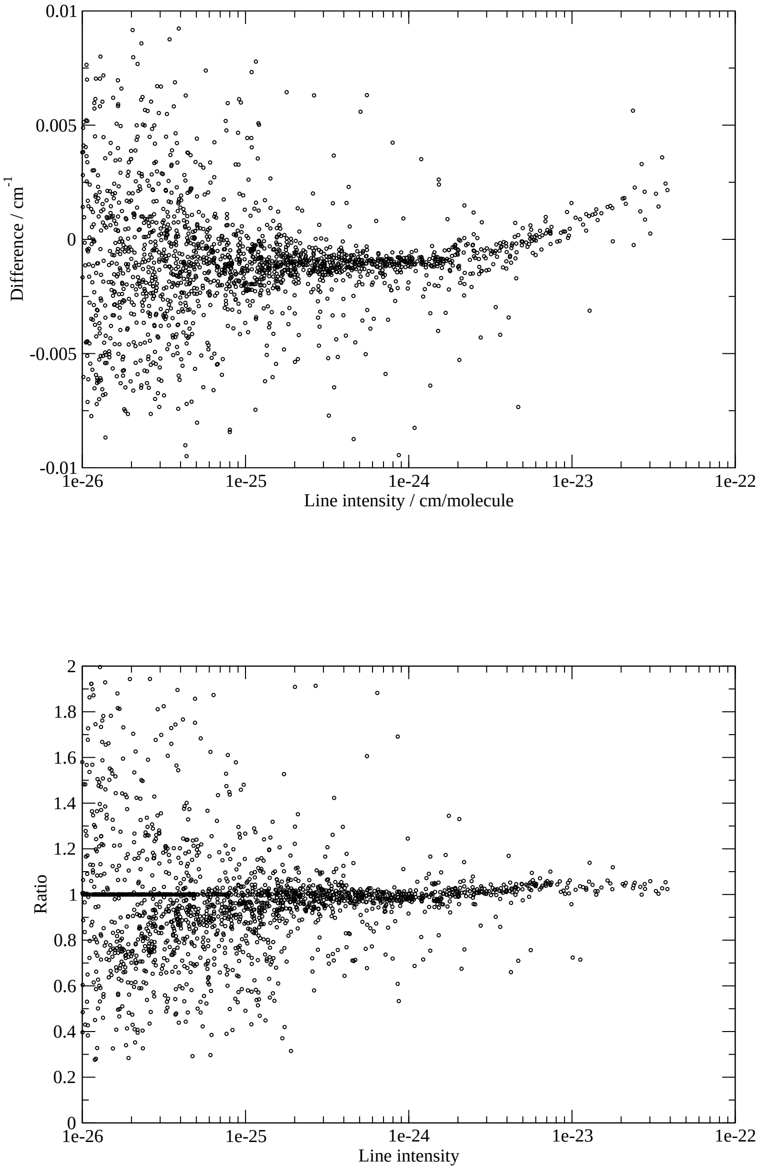


Figure 7: Comparison of the line positions (upper) and line intensities (lower) from this work with those from the HITRAN 2004 database [13] as function of line intensity at room temperature in the range 13000 – 14500 cm^{-1}.

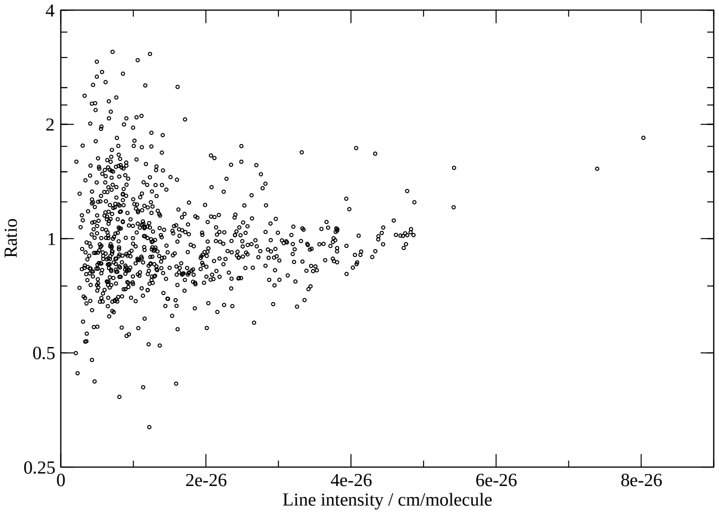


Figure 8: Comparison of the line intensities from this work with those from Mazzotti *et al* [16] as function of line intensity from this work at room temperature in the range 11300 – 12850 cm^{-1}.

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