Pergamon

J. Quant. Spectrosc. Radiat. Transfer Vol. 53, No. 4, pp. 373–380, 1995
0022-4073(94)00131-6

0022-4073/95 $9.50 + 0.00

COMPUTED INFRARED ABSORPTION PROPERTIES OF HOT WATER VAPOUR

JEREMY H. SCHRYBER, STEVEN MILLER, and JONATHAN TENNYSON†
Department of Physics and Astronomy, University College London, Gower Street,
London WC1E 6BT, U.K.

(Received 22 August 1994)

Abstract—Using first principles quantum mechanics we have computed a list of 6.2 million infrared transitions for $H_2^{16}O$. This dataset is used to study the absorption properties of water as a function of temperature between 300 and 3000 K. Comparison is made with experimental data of Ludwig (*Appl. Opt.* **10,** 1057) and the 30,117 lines contained in the HITRAN database. AT 300 K the HITRAN data is the most reliable, but at higher temperatures HITRAN contains too few lines to be useful. Ludwig's data is too coarse to be reliable for many applications and shows a number of systematic errors when compared with our dataset or HITRAN. Methods of further improving our linelist are discussed.

1. INTRODUCTION

The *infrared* spectrum of water is one of the most important and most thoroughly studied. However little reliable data on hot water (above ~1000 K) is generally available. One important source of spectral absorption data is the Ludwig[1] steam data. Ludwig measured the absorption of water in a flame between 1000 and 3000 K and hence tabulated absorption coefficients for water in the temperature range 300–3000 K. Ludwig's experiment was performed at 20 cm^{-1} resolution and he binned his results in 25 cm^{-1} boxes. This data is still widely used for constructing water band profiles,[2–4] atmospheric modelling,[5–7] laser modelling,[8] flame models[9] and analysing the atmospheres of cool stars.[10–16] Although water absorption coefficients have been generated by other workers, for example,[4,17,18] none of these are as comprehensive as Ludwig's and only the earlier work of Ludwig et al[18] probed high temperatures. All these works only used a resolution of 25 cm^{-1}.

Recently we have become interested in the absorption properties of water vapour, our primary motivation being the study of cool stellar atmospheres.[19] To this end we have generated, using first principles quantum mechanics, an extensive list of *infrared* transitions for water which have been used to model the atmosphere of cool M dwarf star VB10.[16] The results for this model using our linelist were dramatically different from results obtained using Ludwig's absorption coefficients. This difference was attributed to the inclusion of much more detailed structure in our linelist compared to the highly smoothed data of Ludwig, and in particular to the resulting gaps between our absorption features which led to a greatly reduced opacity functional at certain key wavelengths.

The differences obtained using our linelist and the Ludwig data were sufficiently striking for us to consider it worthwhile to perform a more detailed comparison. As a control we have also used the 30,117 $H_2^{16}O$ lines available in the HITRAN database.[20] These individually measured lines should give very accurate absorption coefficients at 300 K but the database contains insufficient high lying rotational levels and hot bands to be reliable at higher temperatures.

2. CALCULATION OF THE LINELIST

The water linelist used in this work was generated by direct quantum mechanical calculation of rotation–vibration energy levels, wavefunctions and associated dipole transition strengths. The

---

†To whom all correspondence should be addressed.

energy levels and wavefunctions were obtained using TRIATOM program suite[21] which finds exact, within the Born–Oppenheimer approximation, variational solutions to the triatomic nuclear motion problem.

Energies and wavefunctions were generated using the best then available[22] water potential due to Jensen.[23] Transition intensities were obtained using a specially written Discrete Variable Representation (DVR) program DIPOLE3[24,25] and the dipole surfaces of Wattson and Rothman.[26] Both the potential energy and dipole surfaces were obtained by systematically adjusting *ab initio* surfaces so that they reproduced the results of high resolution spectroscopic studies.

Detailed comparison of *all* the observed vibrational band origins calculated with those calculated using Jensen's potential shows a standard deviation of 6.4 cm^{-1}.[22] However for the bands of interest here, our calculations reproduce the band origins with a standard deviation of only 0.9 cm^{-1}. For low lying rotational levels Jensen's potential reproduces the observed rotational term values with a standard deviation of only 0.14 cm^{-1}[22]; but calculations for high lying rotational states ($J \sim 20$) show errors as large as 10 cm^{-1}.[36] Comparisons of individual linestrengths with those tabulated on the HITRAN database have been performed by Wattson and Rothman[26] and Lynas Gray et al[24] who found that most of the strong transitions were reproduced within the 10% error quoted in HITRAN.

The initial linelist, reported by Miller et al[27] (who give details of the calculations) was extended by Allard et al.[16] It is this linelist that we use in this work. The linelist is based on calculations performed for rotational levels up to $J = 30$. Although convergence was good for states with $J \leqslant 20$ it deteriorated to about 10 cm^{-1} for states with $J = 30$. All levels up to 11,000 cm^{-1} above the ground state are included as well as many, but not all, higher ones. Transitions were calculated using only rigorous selection rules concerning angular momentum ($\Delta J = 0, \pm 1$) and parity.[28] 8.4×10^6 transitions were calculated and 6.2×10^6, with line strengths greater than 10^{-10} D^2, were retained in the linelist used here.

There are a number of ways in which the accuracy and extent of our linelist could be improved which will be discussed below. However at this stage we should note one important defect of our present calculations. For technical reasons due to choice of coordinates in TRIATOM program,[21] our calculations do not distinguish between wavefunctions of ortho and para states of water. In generating total absorption coefficients therefore, we have weighted all transitions with a common nuclear spin degeneracy factor of $g = 2$, rather than the $g = 3$ and $g = 1$ appropriate for ortho and para states, respectively. This approximation is fairly reliable at high temperature as most of the high lying rotational levels come in (near) degenerate ortho–para doublets. However at low temperature this procedure is less reliable.

For this reason we have identified the 25,894 transitions associated with the vibrational ground state in rotational levels up to $J = 10$ and assigned the appropriate ortho/para g weighting. Detailed comparisons with HITRAN data at 300 K showed that this procedure greatly improved our predicted absorption parameters at low temperature but made little difference to results at 3000 K. A similar procedure, i.e., assigning nuclear spin states by hand for a few low-lying levels, was found to give reliable partition functions in a recent study of the thermodynamic properties of H_3^+.[29]

3. ABSORPTION COEFFICIENTS

Starting from the natural abundance weighted transition probabilities, $|R|^2$, tabulated in HITRAN[20] in D^2, we obtained an integrated absorption intensity, in cm^{-2}atm^{-1}, for each transition of frequency ω, in cm^{-1}, using the expression

$$I = C\frac{\omega g(2J'+1)}{Q}\left(\exp\left(\frac{-E''}{kT}\right)-\exp\left(\frac{-E'}{kT}\right)\right)|R|^2, \tag{1}$$

where the constant of proportionality, C, has the value of 11.152 for the particular combination of units and natural abundance used in HITRAN.

Our linelist stores Einstein A coefficients, A_{if}, in s^{-1}. These can be converted into transition probabilities, $|R|^2$, without weighting for isotopic abundance, using the expression

$$|R|^2 = \frac{2J''+1}{2J'+1}\frac{A_{if}}{\omega^3}. \tag{2}$$

Using this $|R|^2$ in Eq. (1) means that the constant, C, takes the value 3.5656×10^7.

In Eq. (1), Q is the partition function. Our partition function was calculated directly from our computed ro-vibrational energy levels by explicit summation

$$Q = \sum_{J,i} (2J + 1) g \exp\left(\frac{-E_{J,i}}{kT} \right), \tag{3}$$

where i runs over all the computed levels with rotational quantum number J, J values considered ran from 0 to 30 and, for reasons discussed above, $g = 2$ for all levels. Our partition function is obtained as a sum over the available calculated levels. As the set of levels is necessary truncated, our value will always be a lower bound on the true partition function. Convergence tests[30] suggest that this error is still less than 1% at 3000 K.

Values of our partition function agree well with those given by other sources, including HITRAN.[20] We note however that this definition of the partition function appears to differ by a factor 4 [or $(2I + 1)^2$] from that generally used by the astrophysics community,[31,32] who appear to neglect the nuclear spin contribution.

As an initial comparison with Ludwig's absorption coefficients, we used both HITRAN and our linelists to generate absorption coefficients binned in boxes of 25 cm^{-1} for a range of temperatures. This binning was done entirely by frequency, ω, and thus ignored the possible effect of the profile of the individual lines. Estimates of both the Doppler and pressure broadening half widths based on the formulae quoted by Phillips[4] show that the Doppler width is very small for temperatures below 3000 K and for pressures of 1 atm or less the self-broadening Lorentz half width is never more than 0.5 cm^{-1}, which can be safely neglected for the box sizes considered here.

Figure 1 shows results for 300 and 3000 K for the entire frequency range considered by Ludwig. At 300 K all three sets of absorption coefficients are similar. However at 3000 K there are significant differences. The absence of high J lines and limited number of bands covered causes systematic gaps in the absorption calculated from the HITRAN database. On the other hand, above about 4000 cm^{-1}, the Ludwig absorption coefficients appear much larger than the others. A discrepancy between the Ludwig results and other measurements of the bands at 1.4 and 1.1 μm has already been noted.[2] We also find a similar mismatch with our calculations of the 1.9 μm band and suggest that Ludwig's results overestimate the absorption coefficient of water over the entire 1–2 μm region at higher temperatures. The only other absorption coefficients available for this region at high temperature, due to Ferriso et al,[18] give results very similar to Ludwig's and will not be considered further here.

Figures 2 and 3 give more detailed comparisons for pure rotation spectrum and the first stretching overtone band at 1.4 μm, respectively. In this case the absorption coefficients generated using HITRAN and our linelist have been binned in 5 cm^{-1} boxes. Comparison of our data with HITRAN for the stretching overtones at 300 K, Fig. 3(a), shows wavelength shifts at both ends of the band. This is due to our calculation being less reliable for the highest rotational states which, as discussed above, are both poorly represented by Jensen's potential and not well converged by our calculations.

The comparisons in Figs. 2 and 3 show up the almost total loss of structure in the coarser Ludwig results. At 300 K the Ludwig data gives a fair average of the absorption coefficient predicted by both HITRAN and us for the pure rotational transitions, Fig. 2(a). However at 3000 K Ludwig's results appear to be blue shifted by up to 100 cm^{-1}, although the general shape and magnitude of the band appears satisfactory.

Ludwig and our results are in reasonable agreement for the fundamental bands so a detailed comparison is not given here. However, for the stretching overtone (Fig. 3) the situation is less satisfactory. At 300 K, the magnitude of the absorption coefficient seems to be similar between the all sets of data, but the peak in the Ludwig data at 7200 cm^{-1} appears at a minimum in the other data. At high temperature, as noted above, the Ludwig data overestimates the absorption although the general shape of the profile is similar to ours. This situation also occurs for the bend-stretch combination band at 1.9 μm.

For diatomic molecules band models have often been generated directly from known linelists. This has not been done routinely for non-linear polyatomic molecules because the number of lines required appear to make such a procedure impractical.[4,33] In the absence of a comprehensive linelist

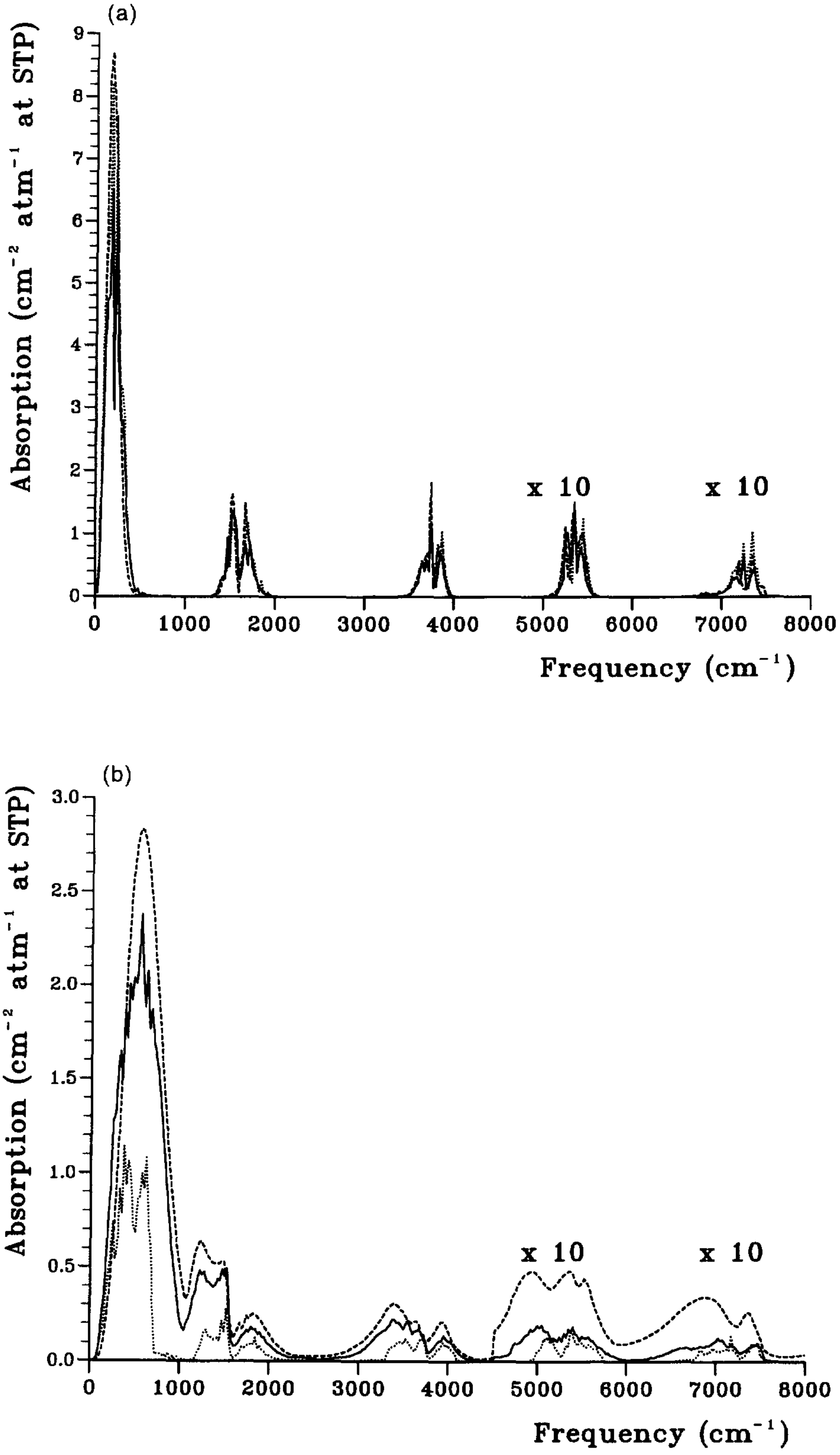

Fig. 1. Comparison of absorption coefficients taken from Ludwig,[1] dashed line; generated using the HITRAN[20] linelist, dotted line, and our linelist, solid line. The absorption coefficients are computed in 25 cm^{-1} bins. The results for frequencies above 4500 cm^{-1} have been scaled by a factor of 10. (a) For a temperature of 300 K and (b) for a temperature of 3000 K.

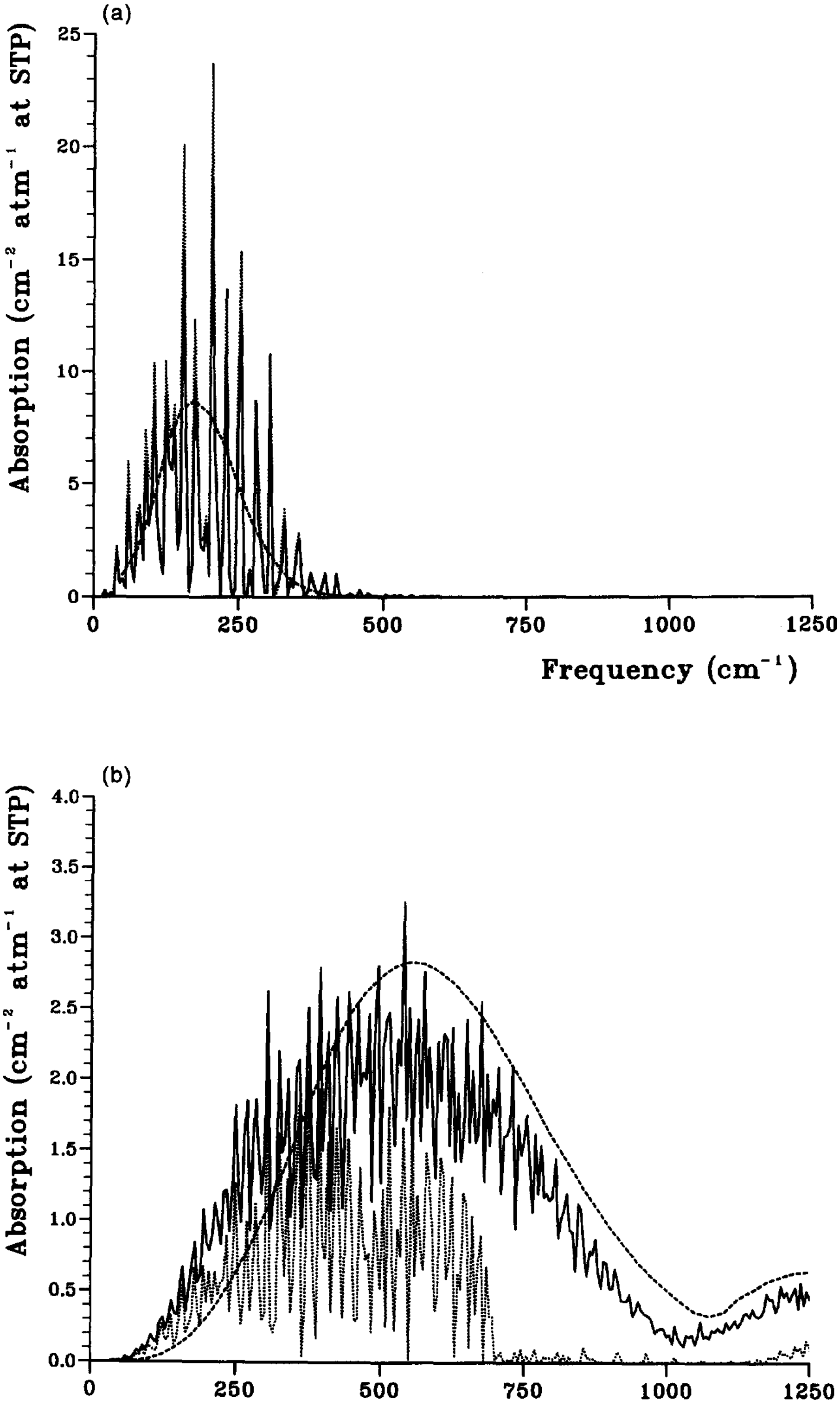

Fig. 2. Comparison of absorption coefficients for pure rotational transitions of water. Results taken from Ludwig,[1] dashed line; generated using the HITRAN[20] linelist, dotted line, and our linelist, solid line. Ludwig's results are for 25 cm^{-1} bins and the others for 5 cm^{-1} bins. (a) For a temperature of 300 K and (b) for a temperature of 3000 K.

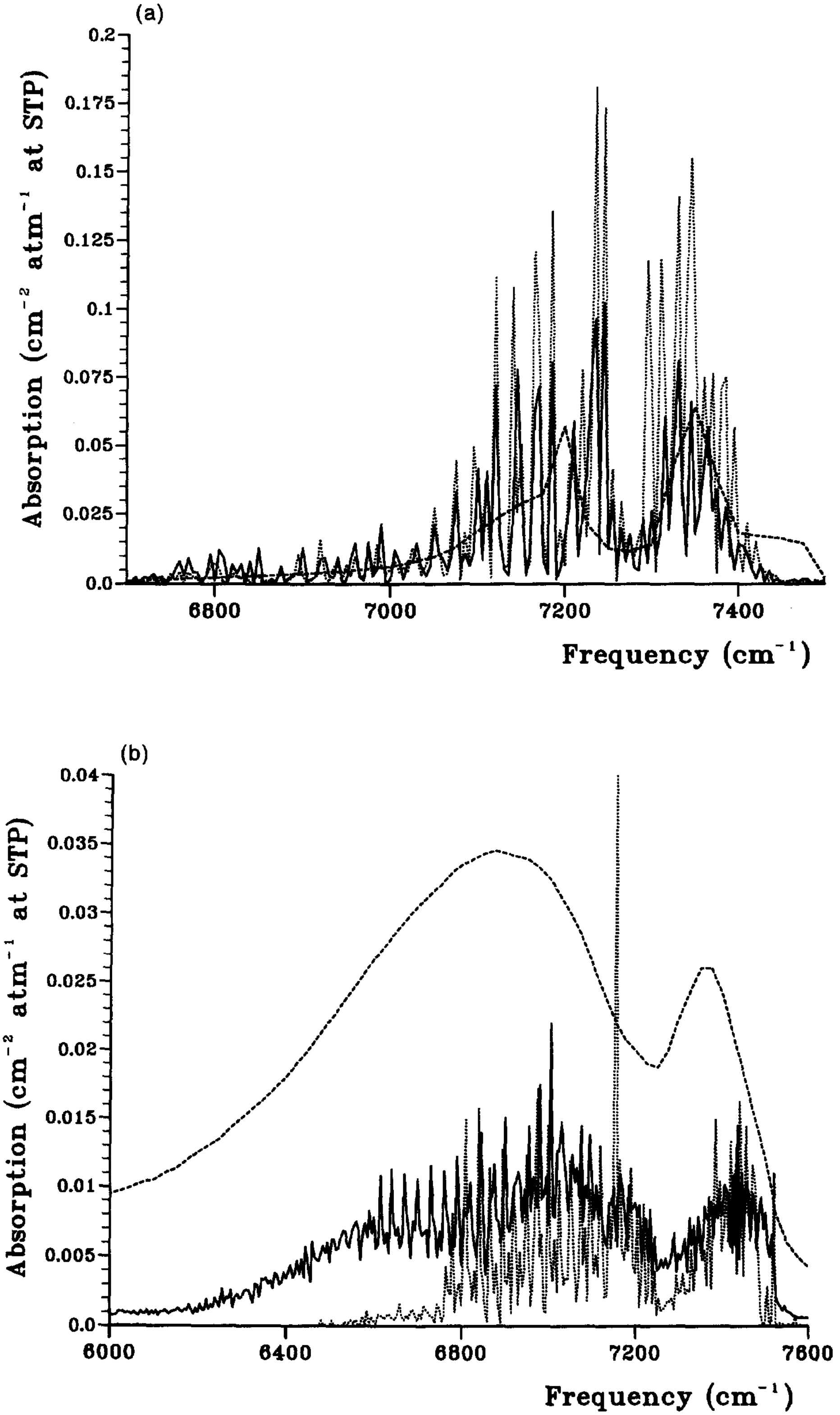

Fig. 3. Comparison of absorption coefficients for the first stretching overtone of water. Results taken from Ludwig,[1] dashed line; generated using the HITRAN[20] linelist, dotted line, and our linelist, solid line. Ludwig's results are for 25 cm^{-1} bins and the others for 5 cm^{-1} bins. (a) For a temperature of 300 K and (b) for a temperature of 3000 K.

for water, sophisticated statistical techniques of generating water band profiles have been developed.[33,34] However such procedures are by their very nature approximate and it is hard to see how they can be reliably extended to high temperatures for which there is little or no experimental data available. In this work we have for the first time used an extensive linelist to generate band profiles for water. Such linelists can in principle be used to generate parameters at arbitrary resolution and temperature.

4. CONCLUSION

We have shown that our linelist can be used to produce the absorption coefficients for water, particularly at high temperature. These coefficients have been compared to those of Ludwig,[1] but can be used in a more flexible and realistic manner to allow for the many gaps that appear in the *infrared* spectra of a light molecule such as water. In addition, using standard formulae (for examples those quoted by Phillips[4]) line profiles can be generated for a range of temperatures, pressures and compositions. A list of 6.2 million lines is too large to publish usefully in the conventional form but the authors will be glad to supply the data in electronic form.†

The linelist used here was our first attempt at the comprehensive treatment of the rotation–vibration spectrum of a triatomic system. There is no doubt that the accuracy and extent of the linelist can be improved. In particular new, significantly more accurate potential energy surfaces for water are now available[35–37] and our new 3D DVR code[25] not only resolves the problem with the ortho–para nuclear spin statistics discussed above, but also should allow us to generate reliable results for higher lying states. We plan to generate a new water linelist in the near future.

Acknowledgements—We thank France Allard and Hugh Jones for helpful discussions. This work has been supported by the U.K. Engineering and Physical Science Research Council and Particle Physics and Astronomy Research Council.

REFERENCES

1. C. B. Ludwig, *Appl. Optics* **10,** 1057 (1971).
2. T. Yamanouchi and M. Tanaka, *JQSRT* **34,** 463 (1985).
3. A. Coppalle and P. Vervisch, *JQSRT* **35,** 121 (1986).
4. W. J. Phillips, *JQSRT* **43,** 13 (1990).
5. L. W. Chaney, *J. Air Pollution Control Ass.* **33,** 220 (1983).
6. A. Yoshida and T. Kunimoto, *Bull. Japan Soc. Mech. Eng.* **26,** 1929 (1983).
7. Y. Abe and T. Matsui, *J. Atmos. Sci.* **45,** 3081 (1988).
8. M. C. Fowler, *AIAA Jl* **19,** 1009 (1981).
9. L. P. Bakhir, G. I. Levashenko, and V. V. Tamanovich, *Combustion Explosion Shock Waves (U.S.S.R.)* **16,** 181 (1980).
10. J. I. Lunine, W. B. Hubbard, and M. S. Marley, *Astrophys. J.* **310,** 238 (1986).
11. M. S. Bessel, J. M. Brett, M. Scholz, and P. R. Wood, *Astron. Astrophys.* **213,** 209 (1989).
12. C. Leinert, M. Haas, F. Allard, R. Wehrse, D. W. McCarthy, J. H. Jahreiss, and C. Perrier, *Astron. Astrophys.* **236,** 399 (1990).
13. S. Sato, K. Okita, T. Yamashita, K. Mizutani, H. Shiba, and H. Takami, *Astrophys. J.* **398,** 273 (1992).
14. H. Shiba, S. Sato, T. Yamashita, Y. Kobayashi, and H. Takami, *Astrophys. J. Suppl.* **89,** 299 (1993).
15. H. R. A. Jones, A. J. Longmore, R. F. Jameston, and C. M. Mountain, *Mon. Not. R. astr. Soc.* **267,** 413 (1994).
16. F. Allard, P. H. Hauschildt, S. Miller, and J. Tennyson, *Astrophys. J.* **426,** L39 (1994).
17. C. B. Ludwig, C. C. Ferriso, W. Malkmus, and F. P. Boynton, *JQSRT* **5,** 697 (1965).
18. C. C. Ferriso, C. B. Ludwig, and A. L. Thomson, *JQSRT* **6,** 241 (1966).
19. S. Miller, J. Tennyson, and J. Fernley, *Rev. Mex. Astrono. Astrofis.* **23,** 63 (1992).
20. L. S. Rothman, R. R. Gamache, R. H. Tipping, C. P. Rinsland, M. A. H. Smith, D. C. Benner, V. M. Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S. T. Massie, L. R. Brown, and R. A. Troth, *JQSRT* **48,** 469 (1992).
21. J. Tennyson, S. Miller, and C. R. Le Sueur, *Computer Phys. Comms.* **75,** 339 (1993).
22. J. A. Fernley, S. Miller, and J. Tennyson, *J. Mol. Spectrosc.* **150,** 597 (1991).
23. P. Jensen, *J. Mol. Spectrosc.* **133,** 438 (1989).
24. A. E. Lynas-Gray, S. Miller, and J. Tennyson, *J. Mol. Spectrosc.* **169,** 6458 (1995).
25. J. Tennyson, J. R. Henderson, and N. G. Fulton, *Computer Phys. Comms.* (in press).
26. R. B. Wattson and L. S. Rothman, *JQSRT* **48,** 763 (1992).

---

†The data is available via our home page on the world wide web accessible on URL http://jonny.phys.ucl.ac.uk/home.html.

27. S. Miller, J. Tennyson, H. R. A. Jones, and A. J. Longmore, *Proc. 146th I.A.U. Colloquium on Molecular Opacities in the Stellar Environment* (Eds P. Thejll and U. G. Jørgenson), pp. 296–309, Springer, Berlin (1994).
28. S. Miller, J. Tennyson, and B. T. Sutcliffe, *Mol. Phys.* **66,** 429 (1989).
29. K. S. Sidhu, S. Miller, and J. Tennyson, *Astron. Astrophys.* **255,** 453 (1992).
30. M. Palao, Final year project, University College London (1994).
31. A. J. Sauval and J. B. Tatum, *Astrophys. J. Suppl.* **56,** 193 (1984).
32. A. W. Irwin, *Astron Astrophys.* **74,** 145 (1988).
33. J. M. Hatmann, R. Levi di Leon, and J. Tain, *JQSRT* **32,** 119 (1984).
34. P. Riviere, S. Langlois, A. Soufiani, and J. Tain, *JQSRT* (**53,** 221–234 (1995).
35. P. Jensen, S. A. Tashkun, and Vl. G. Tyuterev, *J. Mol. Spectrosc.* **168,** 271 (1990).
36. C. D. Paulse and J. Tennyson, *J. Mol. Spectrosc.* **168,** 313 (1994).
37. O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **101,** 7651 (1994).