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Improved near-infrared methane band models and k-distribution parameters from 2000 to 9500 cm^{-1} and implications for interpretation of outer planet spectra

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Abstract

The band model fits of Sihra [1998. Ph.D. Thesis. University of Oxford], subsequently reported by Irwin et al. [2005. Icarus 176, 255–271], to new measurements of low-temperature near-infrared self-broadened methane absorption spectra combined with earlier warmer, longer path measurements of both self- and hydrogen-broadened methane spectra measured by Strong et al. [1993. J. Quant. Spectrosc. Radiat. Transfer 50, 363–429], have been found to contain severe artefacts at wavelengths of very low methane absorption. Although spectra calculated from these new band data appear to be reliable for paths with low to medium absorption, transmissions calculated for long paths of high methane absorption, such as for Uranus, Neptune and Titan are severely compromised. The recorded laboratory transmission spectra of Sihra [1998. Ph.D. Thesis. University of Oxford] and Strong et al. [1993. J. Quant. Spectrosc. Radiat. Transfer 50, 363–429] have thus been refitted with a more robust model and new k-distribution data for both self- and hydrogen-broadened methane absorption derived. In addition, a new model of the temperature dependence of the absorption has been employed that improves the quality of the fit and should also provide more accurate extrapolations to low temperatures.

Keywords: Spectroscopy; Uranus; Titan

1. Introduction

The absorption of methane is very important in the near-infrared spectra of the giant outer planets and Titan. The line data available in databases such as HITRAN (Rothman et al., 2005) and GEISA (Jacquinet-Husson et al., 2005) are improving all the time, but there are still substantial gaps at short wavelengths, particularly of weak lines, which are important in modelling the spectra of these planets. The near-infrared spectrum of methane becomes increasingly complicated at short wavelengths making the assignment of transition lines for line-by-line databases difficult. Until these data sets are completed, those interested in modelling the near-infrared cold temperature spectra of these planets must instead use empirical data or band model parameters (and/or k-distribution fits to these data) fitted to measured transmission spectra of laboratory paths of methane recorded over the temperatures, pressures and path lengths appropriate to outer planet atmospheres. One such set of band model parameters (for self-broadening conditions only) is that of Giver et al. (1990), to which k-coefficients were fitted by Baines et al. (1993). Another set has been measured by collaborators at Oxford University and the Molecular Spectroscopy Facility of the Rutherford Appleton Laboratory (Calcutt, 1984;

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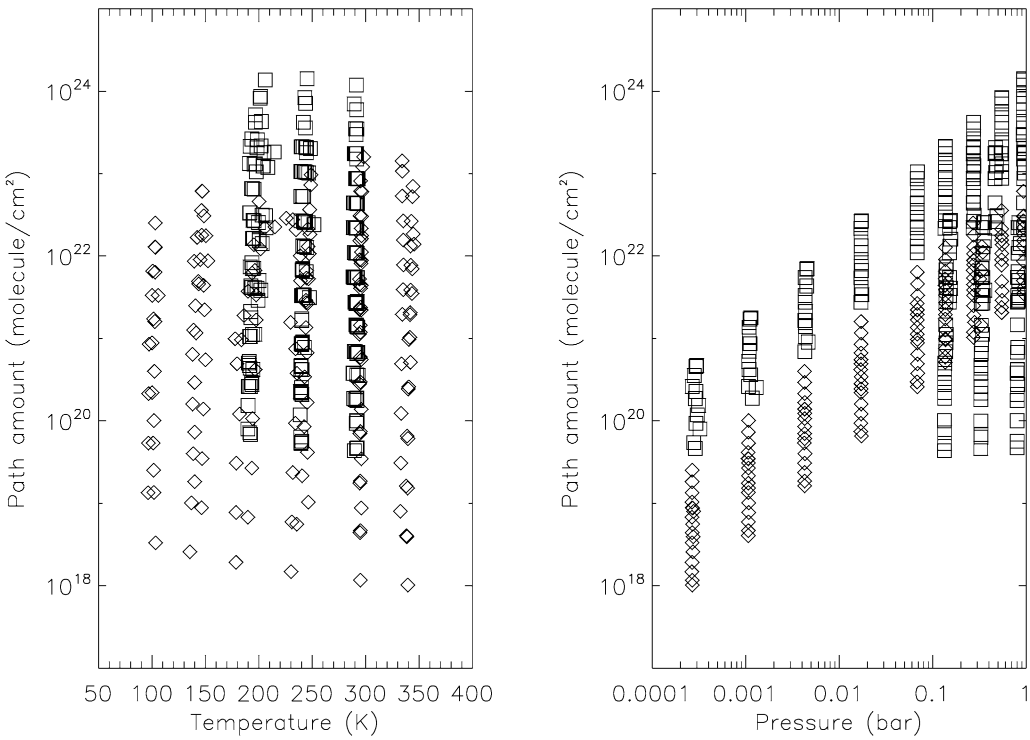

Fig. 1. Measurement conditions of the methane transmission spectra recorded by Strong et al. (1993) (squares) and Sihra (1998) (diamonds).

Strong, 1992; Strong et al., 1993) and k-distribution parameters were fitted to these data by Irwin et al. (1996).

While the methane data of Strong et al. (1993) covered longer path lengths than the data of Giver et al. (1990) and included both self- and hydrogen-broadening, they were only measured down to 190 K, which is considerably warmer than typical conditions in outer planet atmospheres. To address this, Sihra (1998) measured the transmission of short paths of self-broadened methane down to temperatures of 100 K, again at the Rutherford Appleton Laboratory Molecular Spectroscopy Facility. These data were reported by Irwin et al. (2005) together with the band model fits derived by Sihra (1998) to a combination of these data and the longer path length data of Strong et al. (1993). Irwin et al. (2005) also presented k-distribution parameters fitted to these band models, which, it was hoped, would be applicable to radiative transfer studies for all of the giant planets and Titan. The grid of measured pressures, temperatures and path amounts covered by the data of Strong et al. (1993) and Sihra (1998) is shown in Fig. 1.

While these data are found to be adequate for their original purpose, which was to model methane absorption in Jupiter's atmosphere, it has since been discovered that there are some features at weakly absorbing wavelengths which become severe for long, cold paths such as those found in the atmospheres of the ice giants and Titan, causing large spikes to appear in the calculated spectra. Since a particular feature of the Sihra (1998) cold-temperature measurements was the possibility to extend the applicability of the band models of Strong et al. (1993) to colder conditions, it became apparent that the original transmission measurements of both data sets would have to be refitted. In this paper we present the fitting of a new, robust band model to the methane transmission measurements of both Strong et al. (1993) and Sihra (1998), together with derived k-distribution parameter set, which displays none of the shortcomings of the previous band model and has an improved temperature dependence. These new data are shown to be stable for both very long paths and cold temperatures and are better able to account for the variation of absorption with temperature.

2. Previous band model fits to laboratory methane transmission spectra

Sihra (1998) and Strong et al. (1993) both measured the transmission of laboratory paths of methane (with a standard terrestrial isotopic mix) at an original resolution of 0.25 cm^{-1}, from 1800 to 11,500 cm^{-1}. The spectra were subsequently smoothed (to improve signal-to-noise) to a resolution of 10 cm^{-1} with a step of 5 cm^{-1} to satisfy Nyquist sampling. The data at higher wavenumbers than 9500 cm^{-1} suffer from considerable noise and are not described here, while the 1800–2000 cm^{-1} region is well covered by available line data. Hence in this paper we shall discuss the 2000–9500 cm^{-1} range only. The transmission data of Strong et al. (1993) were fitted with a Goody–Voigt band model where the transmission of a path is expressed as

$$T = \exp\left(-2mk_{\tilde{\nu}}(T)\int_0^{\infty}\frac{V(x,y)}{1+m\delta k_{\tilde{\nu}}(T)V(x,y)/(\alpha_D^0\sqrt{T})}\,\mathrm{d}x\right). \tag{1}$$

Here m is the number of absorbing gas molecules per unit area (or path amount), δ is the mean line spacing, $k_{\tilde{\nu}}(T)$ is the mean absorption coefficient, α_D^0 is the mean Doppler line-width at a reference temperature T_0 (296 K), and $V(x, y)$ is the Voigt function as given by Strong et al. (1993). The variable y is the mean ratio of the Lorentz-broadened (i.e. pressure-broadened) to Doppler-broadened line-widths

$$y = \frac{\alpha_L}{\alpha_D} = \frac{\alpha_L^0}{\alpha_D^0}\frac{P}{P_0}\sqrt{\frac{T_0}{T}}\left(q + \frac{(1-q)}{SFB}\right), \tag{2}$$

where α_L^0 is the mean Lorentz line-width at the reference temperature T_0, q is the mole fraction, *SFB* is the mean self-to-foreign broadening ratio, and P_0 is a reference pressure, taken to be 1 atm. The absorption coefficient $k_{\tilde{\nu}}(T)$ is assumed to vary with temperature as

$$k_{\tilde{\nu}}(T) = k_{\tilde{\nu}0}\left(\frac{T_0}{T}\right)^{1.5}\exp\left(1.439E_l\left(\frac{1}{T_0} - \frac{1}{T}\right)\right), \tag{3}$$

where E_l is the mean lower state energy expressed in cm^{-1}, and the temperature exponent is appropriate to describe the rotational partition function of a tetrahedral molecule such as methane (Fox, 1970).

This model may be fitted to laboratory-measured spectra to return five separate parameters: $k_{\tilde{\nu}0}$, δ/α_D^0, α_L^0/α_D^0, E_l, and *SFB*. Sihra (1998) adopted the same band model when fitting to the combined transmission measurements of both his data and Strong et al. (1993), but also added a far-wing continuum correction through an additional transmission term

$$T = \exp\left[-C_1 m\left(\frac{P}{P_0}\right)\left(\frac{T}{T_0}\right)^{C_2}\right], \tag{4}$$

where the coefficients C_1 and C_2 are two extra fitting parameters.

Another difference of the new analysis was that Sihra (1998) found the self-to-foreign broadening ratio *SFB* fitted by Strong et al. (1993) to be under-constrained, allowing physically unrealistic variations of *SFB* to be derived in compensation for fitting of other parameters. Instead of fitting this parameter at each wavelength, Sihra (1998) derived a band-averaged *SFB* factor for hydrogen-broadening of 1.40 ± 0.07 by comparing fits to both self- and hydrogen-broadened spectra. This factor is found to be consistent with the self- to air-broadened methane line widths of the most recent line listings of GEISA and HITRAN: in the 2000–3000 cm^{-1} region, the mean strength-weighted 10-cm^{-1} resolution ratio of self-broadened to air-broadened widths is found to be 1.41 ± 0.07, while in the 3500–4500 cm^{-1} region it is found to be 1.29 ± 0.03, both of which should be increased by about 8% to compare with ratios involving hydrogen as the foreign gas (Benesch and Elder, 1953), making them reasonably consistent with the Sihra (1998) result. An additional confirmation of the assumed *SFB* factor comes from the analysis of broadening of methane lines by a number of gases near 3000 cm^{-1} by Pine (1992), who found N_2 and H_2

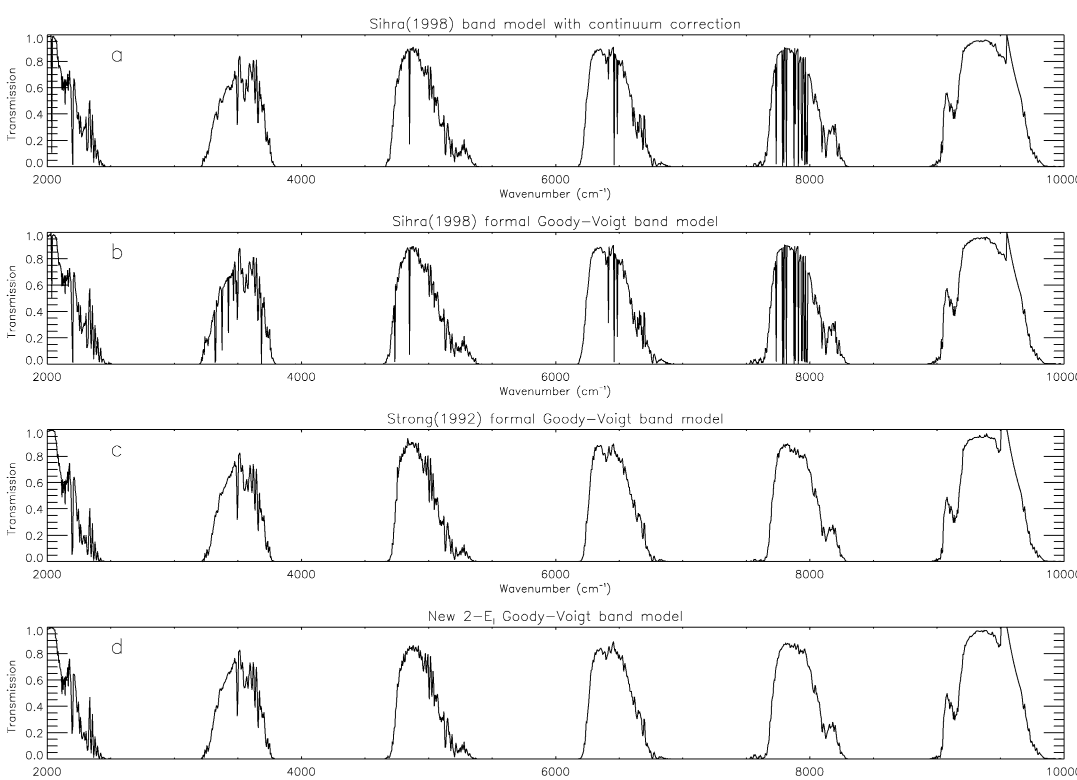

Fig. 2. Calculated transmission of methane for a typical Uranus path at pressure 0.933 bar, temperature 240 K, containing 0.5446 km-amagat (1.462×10^{24} molecules/cm^2) of methane using different sources of methane band data: (a) Sihra (1998), including continuum correction, (b) Sihra (1998), excluding continuum correction, (c) Strong et al. (1993), and (d) new fitted band model to combined transmission measurements of Strong et al. (1993) and Sihra (1998).

broadening to be similarly effective and derived a self- to N_2-broadening factor of 1.25 ± 0.04.

While the band model parameters of Sihra (1998) were found by Irwin et al. (2005) to model jovian conditions well, Fig. 2 shows that the calculated transmission of methane for a typical Uranus path at pressure 0.933 bar, temperature 240 K, containing 0.5446 km-amagat (1.462×10^{24} molecules/cm^2) of methane, has spurious spikes appearing in regions of low absorption, especially at 8000 cm^{-1}. Initially it was thought that this might be due to the additional temperature factors of Sihra (1998). The Goody–Voigt band model is based on the known behaviour of absorption lines, assuming a random distribution, and should be equally applicable at all temperatures. However, while the extra temperature factors of Sihra (1998) were found to improve the fit to the data, they are semi-empirical in nature and thus of unknown reliability when extrapolated to conditions outside of those measured. Sihra (1998) also fitted the formal Goody–Voigt model to the combination of his and Strong et al.'s (1993) data, but the transmission spectrum calculated from these fits, shown in Fig. 2, also displays spurious spikes. In contrast, the transmission calculated using the Goody–Voigt band model parameters of Strong et al. (1993) (fitted only to their longer path, 190 to 296 K spectra) has no such spikes and appears well behaved.

3. New band model fits to laboratory methane transmission spectra

It was clear that a fundamental problem had arisen in the fitting process used by Sihra (1998) and thus that the original self-broadened transmission measurements of both Sihra (1998) and the self- and hydrogen-broadened measurements of Strong et al. (1993) needed to be refitted. Previous attempts at fitting band data have found that the process is finely balanced and sensitive to initial conditions. To achieve a reliable fit, a suite of models have been successively fitted, each one serving as the basis for the next, in order not to allow too much 'play-off' between the different parameters. To refit the data, it was decided to use experience gained from retrieving atmospheric profiles from remotely sensed infrared spectra and use a constrained fit, where an a priori 'guess' is used as the starting condition combined with an appropriate amount of constraint to avoid the fitted parameters having too much freedom. To do this we used the approach of nonlinear optimal estimation (Rodgers, 1976, 2000), where the next iterated estimate of the model vector $\mathbf{x}$ (in this case the band parameters) is determined from

$$\mathbf{x}_{n+1} = \mathbf{a} + \mathbf{S}_x \mathbf{K}_n^{\mathrm{T}} \left(\mathbf{K}_n \mathbf{S}_x \mathbf{K}_n^{\mathrm{T}} + \mathbf{S}_\varepsilon\right)^{-1} \left(\mathbf{y} - \mathbf{y}_n - \mathbf{K}_n(\mathbf{a} - \mathbf{x}_n)\right), \tag{5}$$

where $\mathbf{K}_n$ is the Jacobian matrix containing the first derivatives of the nth calculated transmission spectrum $\mathbf{y}_n$ with respect to all the elements in the state vector $\mathbf{x}$, $\mathbf{a}$ is the a priori estimate of the band parameters, and $\mathbf{S}_x$ and $\mathbf{S}_\varepsilon$ are the assumed covariance matrices of the band parameter vector and measured transmission spectrum $\mathbf{y}$, respectively. For this case, both covariance matrices are assumed diagonal. For stability, the next iterated value of the state vector $\mathbf{x}$ in Eq. (5) was 'braked' using a Marquardt–Levenburg scheme (Press et al., 1992) and to ensure positive values for the fitted band parameters, the log of the parameters was fitted by the model.

Using this scheme the measured transmission data were initially fitted with the formal Goody–Voigt model alone, excluding the continuum correction of Sihra (1998), although, as recommended by Sihra (1998), the *SFB* factor was fixed at 1.4. Two a priori sets of band data were used to constrain the model: (1) the band model fits of Strong et al. (1993), and (2) band parameters derived from the methane line data downloaded from the GEISA 2003 website, which are described by Brown et al. (2003) and Brown (2005). The transmission spectra were assumed to have an error of 0.05 and a number of retrieval tests were run using varying levels of constraint on the individual elements of the a priori measurement vector, varying from $\Delta x/x = 0.02$ to $\Delta x/x = 20$ (the a priori error of all band parameters was assumed to be the same). With too much constraint, the retrieved band parameters did not vary far from the initial guess and the resulting calculated transmissions did not fit the spectra well. With too little constraint, the spectra were well fitted, but the fitted parameters were not well behaved, varying wildly from one wavelength to the next. It was found that a good trade-off was achieved by setting $\Delta x/x = 2.0$, which also corresponded to the elements of the leading diagonal of the matrix $\mathbf{K}_n \mathbf{S}_x \mathbf{K}_n^{\mathrm{T}}$ being of the same order of magnitude as the diagonal elements of the measurement covariance matrix $\mathbf{S}_\varepsilon$, indicating a good balance between a priori constraint and measurement error. In addition, for this choice of constraint, the fitted parameters using the two different choices of a priori band parameters were very similar to each other and were thus not overly dependent on the initial guess. The re-fitted Goody–Voigt band model parameters are shown in Fig. 3.

While the Goody–Voigt model fits the transmission spectra well, there are some differences especially at intermediate temperatures. This can be seen in Fig. 4, where for the transmissions measured at 4100 cm^{-1}, the difference between the measured and fitted transmissions has been plotted as a function of temperature, pressure and path amount. It can be seen that while the difference between measured and fitted transmission is small at 100 and 300 K, there is a trend to slightly underestimate the transmission at around 200 K. The Goody–Voigt band model assumes that all the lines in a particular averaging bin have the same variation of absorption with temperature, due primarily to the lower state energy parameter E_{l}. However, in practise lines of different strength in an interval may have very different lower state energies, and thus temperature dependence. To address this Sromovsky et al. (2005) proposed using a band model where the absorption strength was calculated as a function of *two* lower state energies E_1 and E_2:

$$k'_{\tilde{\nu}}(T) = a k_{\tilde{\nu}}(T, E_1) + (1 - a) k_{\tilde{\nu}}(T, E_2), \tag{6}$$

where $k_{\tilde{\nu}}(T)$ is the function defined in Eq. (3) and were a is a weighting parameter, whose value may vary between 0 and 1. Simulations by Sromovsky et al. (2005) showed that this formalism improves the accuracy of fit at intermediate temperatures and also provides more accurate extrapolations below

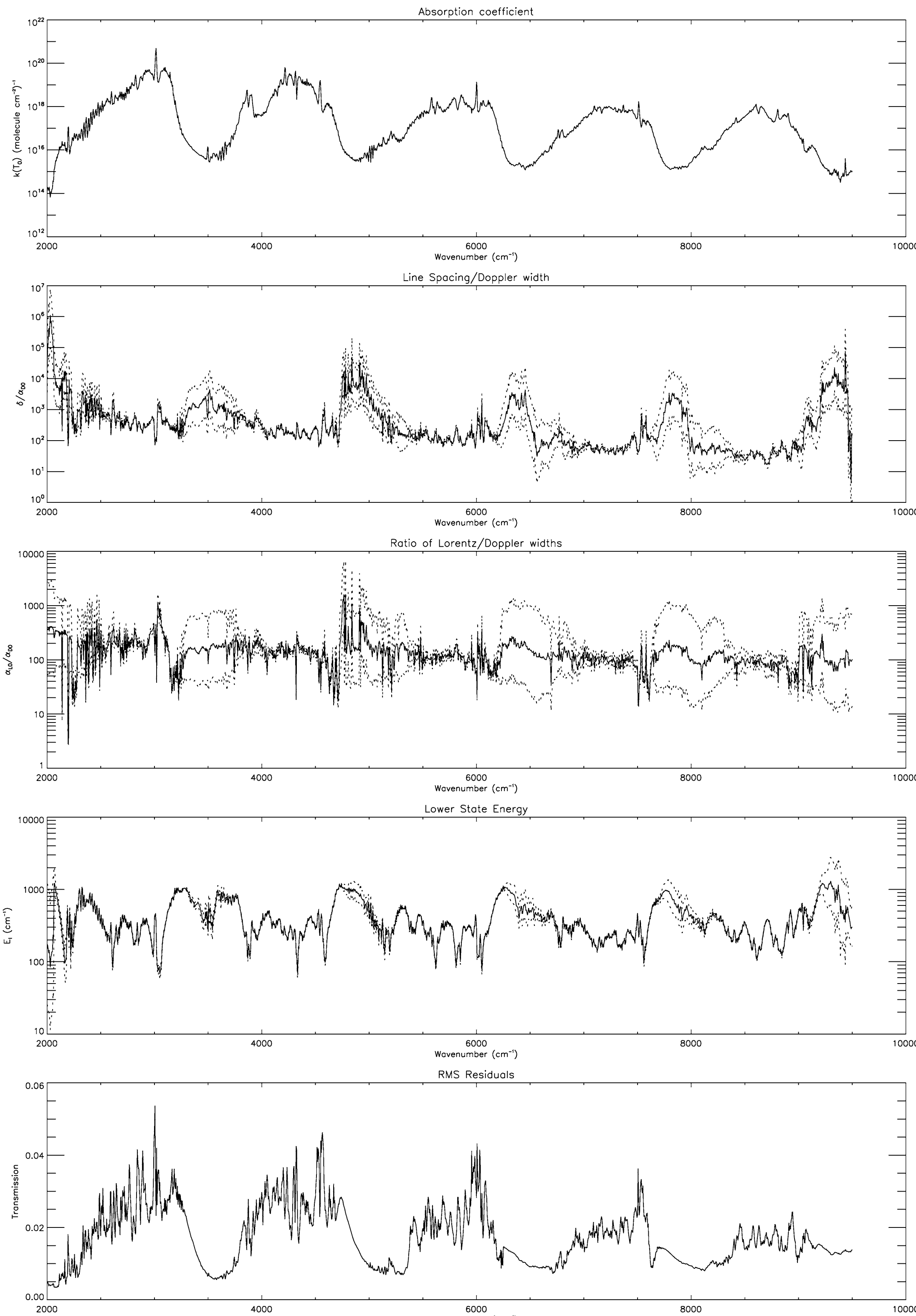

Fig. 3. Fitted Goody–Voigt band parameters and r.m.s. fitting error to laboratory-measured methane transmission spectra using a single-E_1 model. Here the solid lines are the fitted parameters and the dotted lines are the confidence limits.

100 K. The Goody–Voigt band model was modified to incorporate this new evaluation of $k'_{\tilde{\nu}}(T)$ and the new parameters: a, E_1, and E_2 added to the measurement vector. The data were refitted and a great improvement in the accuracy of the fits was indeed achieved, especially at intermediate temperatures, with the overall χ^2 decreasing at some wavelengths by a factor of almost 2. It was further found that allowing the parameter a to vary did not greatly improve the fits and thus, to reduce the

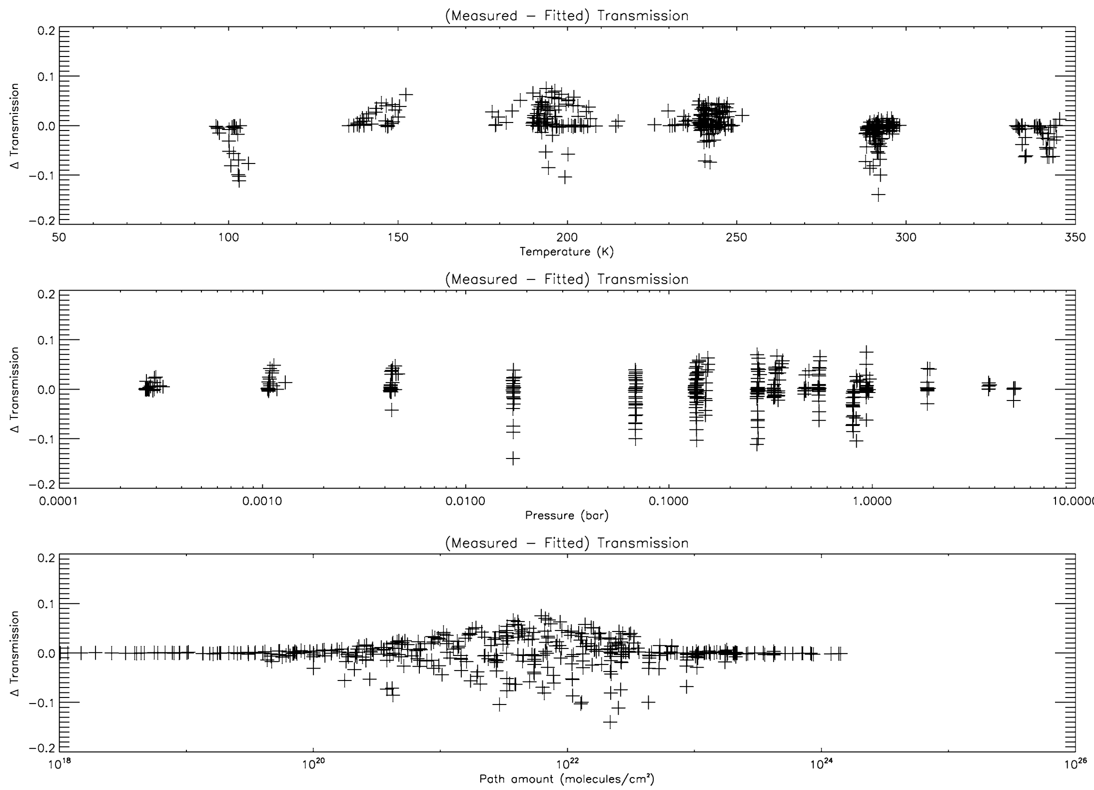

Fig. 4. Difference between measured and fitted transmissions at 4100 cm^{-1} as a function of temperature, pressure and path amount, using the original single-E_l Goody–Voigt band model. The model appears to underestimate the transmission at intermediate temperatures.

number of free parameters, this parameter was subsequently fixed to a value of 0.5.

Fig. 5 shows the derived band parameters and r.m.s. fitting error for the new 2-E_l band model, and Fig. 6 shows the difference between the measured and fitted transmissions at 4100 cm^{-1}, where a clear improvement can be seen, especially at intermediate temperatures. Hence this formulation of the band model was adopted as being more accurate and reliable. Table 1 lists a small section of the newly retrieved band parameters around 8100 cm^{-1} while Table 2 lists the band parameters of Strong et al. (1993) in the same region for comparison.

Once a reliable set of band model parameters had been derived, k-distribution parameters were fitted to the models as previously described by Irwin et al. (1996, 2005). The transmission curves fitted by the k-coefficients were found to be accurate to better than 0.5% in most cases, with maximum fitting errors of only 2.5%—well within the accuracy of the band-modelled transmission curves themselves. The k-tables have been tabulated at 20 pressures (logarithmically spaced) between 1×10^{-6} and 10 bars, and 19 temperatures between 50 and 410 K, in steps of 20 K. Ten g-ordinates have again been used (Irwin et al., 2005). The k-tables and band parameters are available from the web site listed at the end of this paper.

4. Discussion

The original band parameters of Sihra (1998) were used by Irwin et al. (2005) to construct k-distribution tables and reanalyse previous NIMS determinations of the jovian cloud structure. The revised band parameters and resulting k-distribution parameters presented here are found to predict spectra which are negligibly different under jovian conditions to the spectra of Irwin et al. (2005) and thus the conclusions of that paper concerning the cloud structure of Jupiter are unaffected.

The shortcoming of the band parameters of Sihra (1998) only presented themselves under much longer, colder paths than occur in the jovian atmosphere, as was seen earlier in Fig. 1. The transmission of that path, calculated using the refitted band parameters, is also shown in Fig. 1 and it can be seen that the spurious spikes have now been removed and thus that the new band parameters appear well-behaved. To explore the revised data further, the band model parameters were used to calculate the transmission of various planetary and laboratory paths and compared with line-by-line calculations. The methane line data in the most recent versions of GEISA (Jacquinet-Husson et al., 2005) and HITRAN (Rothman et al., 2005), whose strengths and lower state energies are plotted in Fig. 7, are described by Brown et al. (2003) and Brown (2005). From 1.1 to 2.1 μm (4760–9010 cm^{-1}) the methane line data are the empirical near-infrared lines of Brown (2005), who estimates the lower state energy to be 555.555 cm^{-1} for lines in the 3800–4600 and 5500–6185 cm^{-1} regions, and 333.333 cm^{-1} otherwise, with both values appearing between 6180 and 6185 cm^{-1}. The compilers of the GEISA have reported these lower state energies directly. However, since these are estimated rather than measured lower state energies, the HITRAN compilers have set the lower state energy of these lines to −1. Now, in order to calcu-

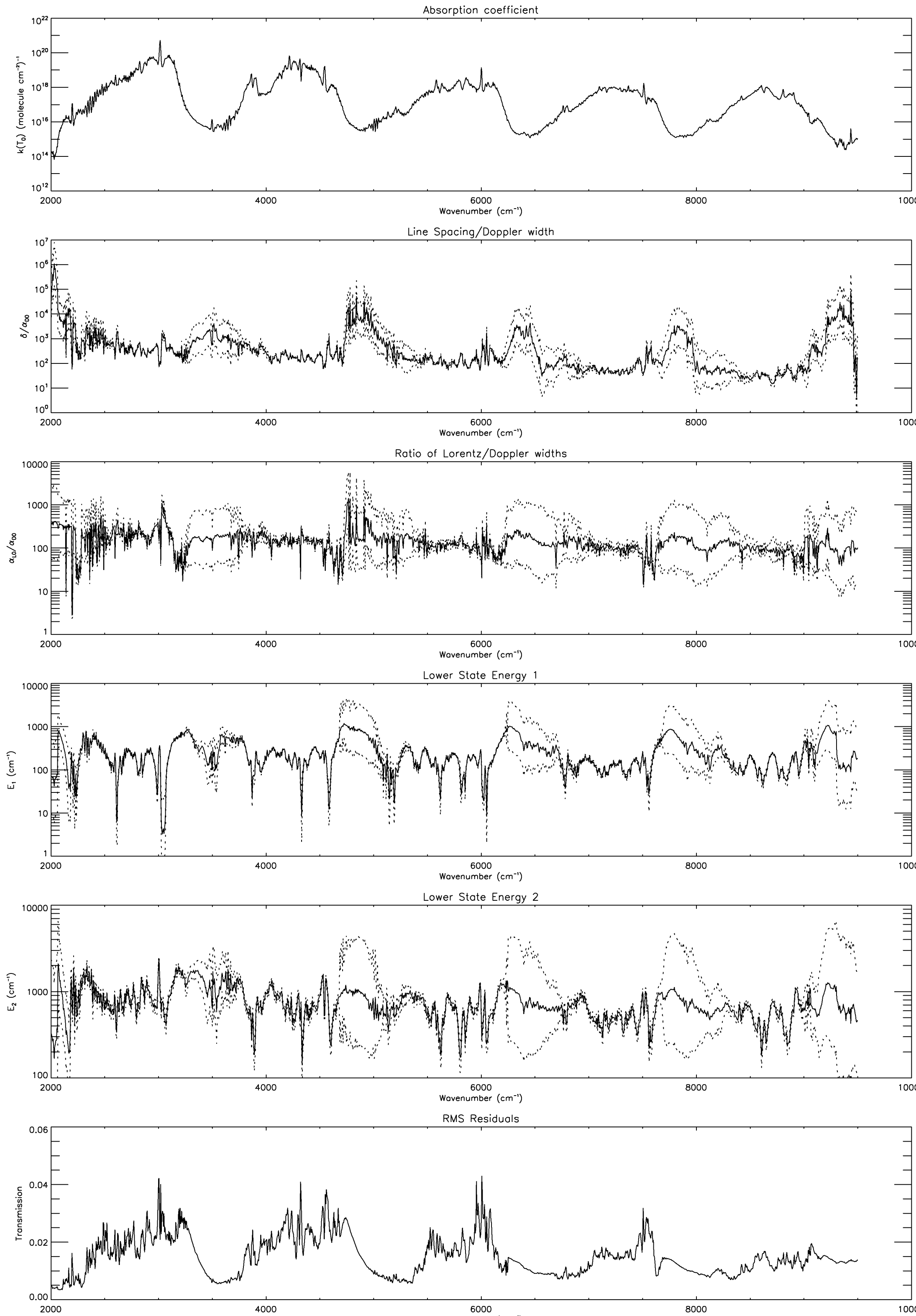

Fig. 5. Fitted band parameters to laboratory-measured methane transmission spectra using the new double-E_1 model. It can be seen that the residuals are significantly less than for the single-E_1 model shown in Fig. 3.

late the methane transmission at low temperature, an estimate of the lower state energy is essential so that the line strength can be scaled in the same way as band model strengths are scaled in Eq. (3). Thus, the new HITRAN methane data on their own cannot be used for modelling methane absorption in outer planet atmospheres. Also plotted in Fig. 7 are the two parts of the lower state energy, E_1 and E_2, fitted to the laboratory transmissions presented here and it can be seen that these

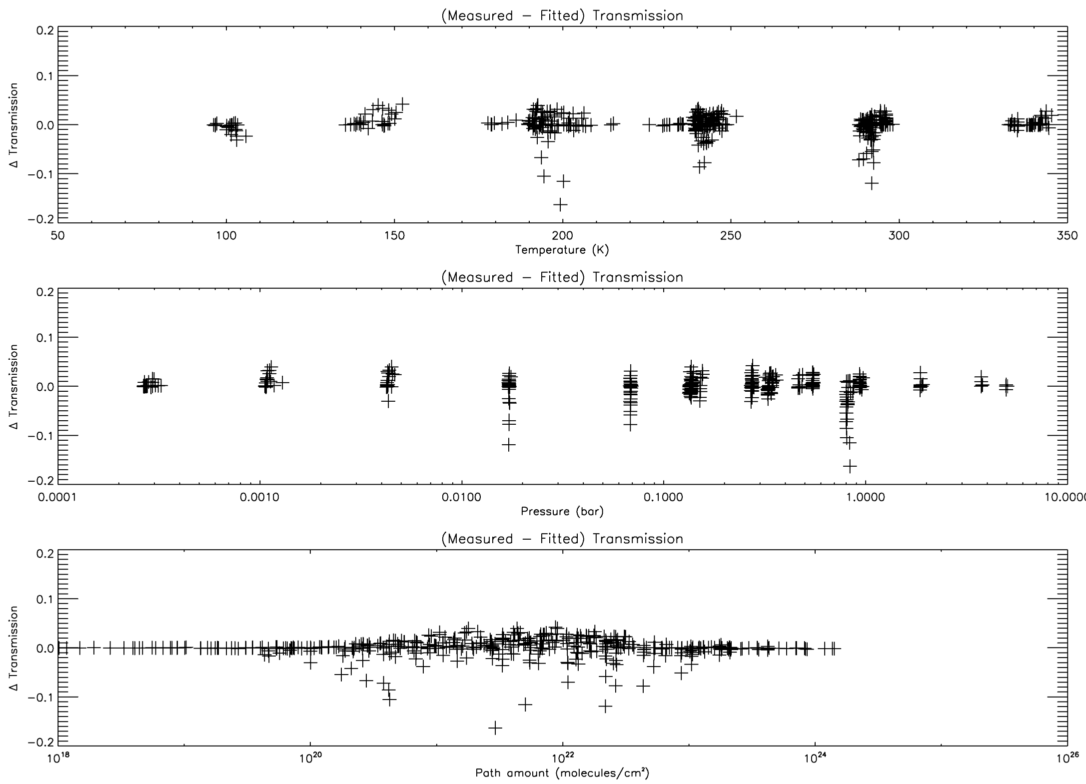

Fig. 6. Difference between measured and fitted transmissions at 4100 cm^{-1} as a function of temperature, pressure and path amount, using the new double-E_l Goody–Voigt band model. The model appears to fit the temperature dependence of the measured data much better.

Table 1
Extract of new fitted band data from 8050 to 8150 cm^{-1}

$\tilde{\nu}$ (cm^{-1})	$k_{\tilde{\nu}0}$ ($\times 10^{20}$ $molecule^{-1}$ cm^2)	δ/α_D^0	α_L^0/α_D^0	E_1 (cm^{-1})	E_2 (cm^{-1})	*SFB*
8050.00	5.26339E−05	56.2958	90.7659	244.984	588.750	1.40000
8055.00	5.28015E−05	67.1672	91.0120	249.987	598.269	1.40000
8060.00	5.74643E−05	72.7703	87.7939	196.316	569.612	1.40000
8065.00	6.25498E−05	55.6450	89.1927	196.890	560.067	1.40000
8070.00	6.25534E−05	53.2859	93.5993	217.948	570.563	1.40000
8075.00	6.57109E−05	78.6885	92.5147	223.450	611.576	1.40000
8080.00	7.80884E−05	82.5072	87.2998	157.501	578.939	1.40000
8085.00	8.43116E−05	59.8539	91.4787	130.913	550.794	1.40000
8090.00	9.33885E−05	61.8211	85.0030	148.605	569.132	1.40000
8095.00	0.000126483	41.6903	64.7814	133.876	509.490	1.40000
8100.00	0.000130356	34.4465	47.5195	151.112	540.853	1.40000
8105.00	0.000105931	52.2824	75.3284	225.086	594.531	1.40000
8110.00	0.000104519	46.2761	86.7843	207.661	558.442	1.40000
8115.00	0.000113509	44.7776	90.7683	161.548	522.560	1.40000
8120.00	0.000130950	47.4629	89.8172	122.863	485.151	1.40000
8125.00	0.000148094	50.5831	106.653	97.0265	469.236	1.40000
8130.00	0.000140263	42.4899	88.8446	110.517	516.867	1.40000
8135.00	0.000128466	43.8999	84.0554	131.921	522.478	1.40000
8140.00	0.000120944	40.6077	80.5897	169.895	510.219	1.40000
8145.00	0.000111416	33.3514	100.876	210.486	509.929	1.40000
8150.00	0.000105649	41.6577	97.3170	206.051	529.330	1.40000

mostly straddle the 555.555 and 333.333 cm^{-1} values assumed by Brown (2005) in the near-infrared, indicating that these are reasonable approximations.

The calculated transmission of various laboratory and planetary paths using the newly revised methane line data of GEISA are compared with the transmissions calculated using the new band data in Fig. 8. In this figure the top plot shows the calculated transmission of the longest path of self-broadened methane measured by Strong et al. (1993) [pressure 0.926 bar, temperature 245.9 K, path length 512.75 m (1.416×10^{24} $molecules/cm^2$ or 0.527 km-amagat)]. The solid line shows the transmission calculated with the band parame-

Table 2
Extract of Strong et al. (1993) band data from 8050 to 8150 cm^{-1}

$\tilde{\nu}$ (cm^{-1})	$k_{\tilde{\nu}0}$ ($\times 10^{20}$ $molecule^{-1}$ cm^2)	δ/α^0_D	α^0_L/α^0_D	E_1 (cm^{-1})	*SFB*
8055.00	5.43600E−05	79.0050	90.3620	397.940	0.299500
8060.00	5.92360E−05	87.6790	88.4250	351.790	0.801300
8065.00	6.43470E−05	65.0900	89.5080	348.530	2.21030
8070.00	6.45460E−05	63.6690	89.6780	367.370	1.06040
8075.00	6.79710E−05	94.1540	91.0360	384.160	0.589820
8080.00	8.09870E−05	100.280	90.3240	327.570	1.89340
8085.00	8.73130E−05	71.2510	89.7000	302.160	1.68680
8090.00	9.68110E−05	75.9700	89.2710	319.700	2.52760
8095.00	0.000130650	59.6260	89.1490	294.310	1.46990
8100.00	0.000134660	62.3750	88.3390	317.420	1.64790
8105.00	0.000109490	68.9540	89.4520	380.930	1.40480
8110.00	0.000108150	56.4570	88.8150	356.910	1.51690
8115.00	0.000117820	52.9480	90.6510	315.750	3.17210
8120.00	0.000136060	54.3540	88.6180	277.940	2.52420
8125.00	0.000153210	57.4610	105.490	254.990	1.98390
8130.00	0.000144710	47.6720	87.9090	277.420	2.20100
8135.00	0.000132790	52.4680	88.3310	295.020	1.54520
8140.00	0.000126060	53.7480	87.4400	319.160	0.844260
8145.00	0.000116460	41.6830	87.8780	344.930	1.09990
8150.00	0.000110210	50.7860	88.3270	347.420	1.37450

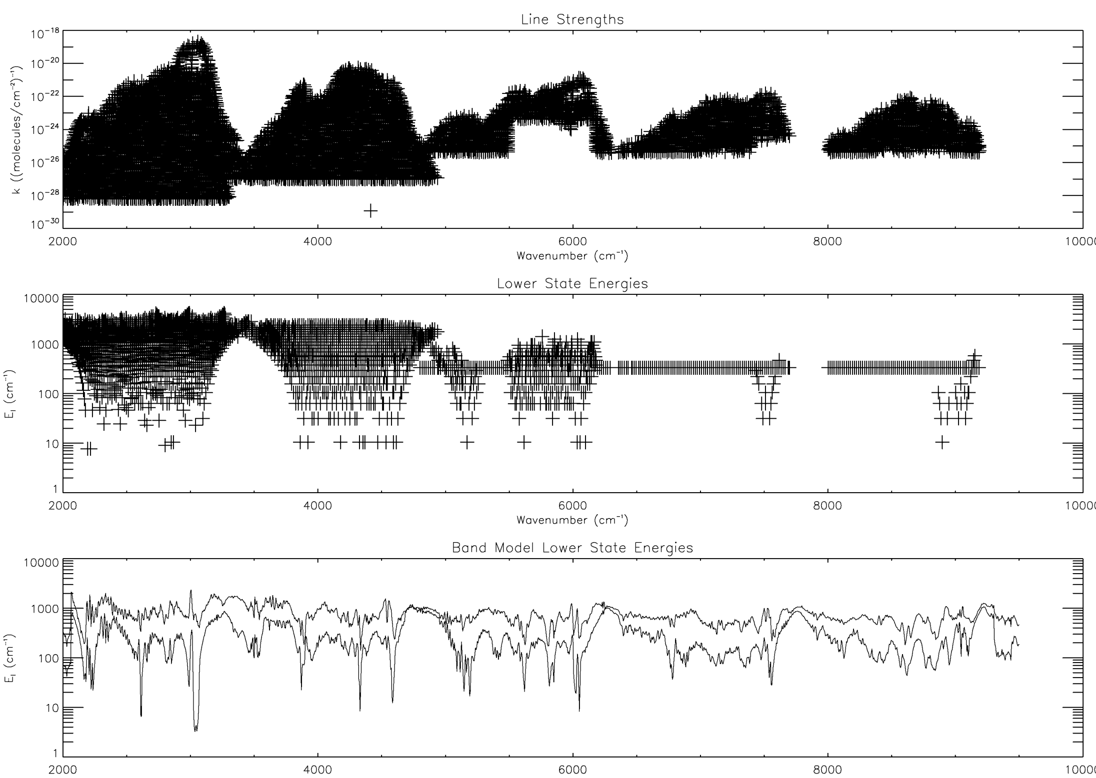

Fig. 7. Methane line strengths and lower state energies downloaded from the GEISA 2003 web site. The lines include the empirical near-infrared lines reported by Brown (2005) for which the lower state energy has been estimated to be either 555.555 or 333.333 cm^{-1}. In the latest version of HITRAN, these lower state energies have been reset to −1, making it difficult to use these data at low temperatures. Shown in the bottom plot for comparison are the fitted band model lower state energies, E_1 and E_2 of the newly fitted band model, which can be seen to be consistent with the range of lower state energies listed in the line data base.

ters presented here, while the dotted line shows the GEISA line-by-line calculation (the difference between the laboratory measured spectrum and band-model fit is negligible at this scale). The effect of the absence of weak lines in the line database between band centres is clear, with the line-by-line model generally predicting more transmission than is observed. The second plot shows the calculated transmission from space to the 1 bar level in Uranus' atmosphere, assuming no clouds and only methane line absorption and collision-induced absorption of H_2–H_2 and H_2–He (Borysow, 1991, 1992), while the third

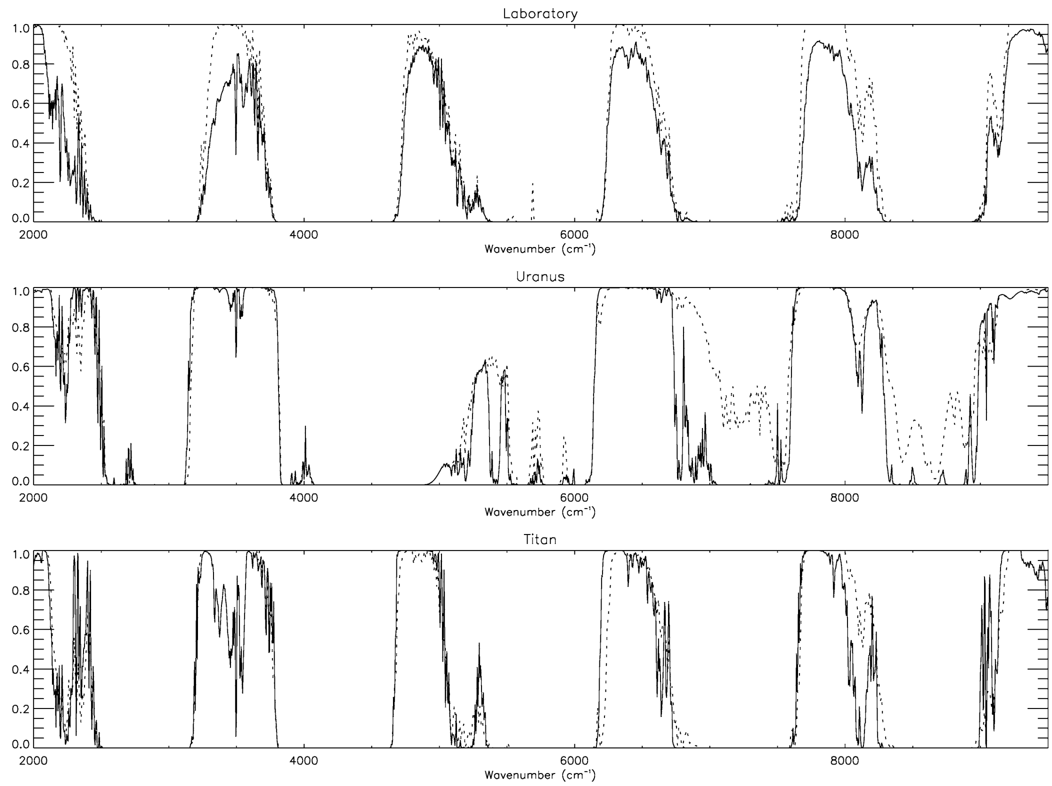

Fig. 8. Calculated transmissions of various paths using the new band data (solid lines) and the methane line data of the most recent GEISA database (dotted lines). The top plot shows the calculated transmission of the longest laboratory path measured by Strong et al. (1993). The second plot shows the transmission from space to the 1 bar level of a nominal Uranus atmosphere, assuming only methane and H_2–H_2, H_2–He collision induced absorption, and no clouds. The third plot shows the calculated transmission from space to the surface of Titan, again assuming no clouds and only methane absorption.

plot shows the calculated transmission from space to the surface of Titan, assuming methane line absorption only. For the Uranus path, the methane was set to be saturated above the condensation level at ~1.1 bar, with a temperature profile derived from Voyager IRIS. The path had a mean pressure and temperature of 0.494 bar and 62.5 K respectively and the path amount of methane was 6.3×10^{23} molecules/cm^2 (0.235 km-amagat). For the Titan path, the temperature profile was again taken from Voyager IRIS estimates and the deep volume mixing ratio of methane set to 4.4% at the ground, reducing to 1.9% in the stratosphere. The mean pressure and temperature of the path were 0.725 bar and 84.4 K respectively and the path amount of methane was 8.2×10^{24} molecules/cm^2 (3.05 km-amagat). The mean pressures of these paths are well covered by the transmission measurement conditions shown in Fig. 1. The path amount for the Uranus atmosphere is also within the range measured, while the Titan path is slightly longer. In both cases, however, the mean temperature is significantly below the minimum measured temperature of 100 K. However, we showed earlier that the 2–E_1 band model used here significantly improves the fit to the measured transmissions and the wavelengths where there is significant discrepancy between the line-by-line and band model calculations are those where the transmission curve is well measured, and thus where the retrieved errors of E_1 and E_2 (shown in Fig. 5) are small. Hence we are as confident as we can be that the extrapolation to colder temperatures is reliable.

As a final indicator of the reliability of extrapolating these data to lower temperatures, Sromovsky et al. (2005) have used these band data to simulate laboratory spectra of methane recorded by McKellar (1989) at 77 K from 1.1 to 2.6 µm, and find good agreement between the calculated and measured spectra. In addition, the new band data are far more successful at reproducing the observed spectrum of Uranus, recorded by Fink and Larson (1979) than other sources of methane opacity.

5. Conclusion

Although the band data presented here are not at very high resolution, they cover a wide range of pressures, temperatures and path lengths. The band model, and derived k-distribution, parameters have been fitted to a high degree of accuracy using a new fitting scheme, and have improved temperature dependence over previous band data. Given the uncertainty in the lower state energies of methane in the GEISA and HITRAN databases, and the absence of weaker lines, especially at short wavelengths, line-by-line calculations of methane transmission at the cold temperatures and long path lengths found in outer planet atmospheres are subject to considerable error. Hence these band data and the k-distribution data derived from them, remain for the moment probably the most reliable way of estimating the near-infrared transmission of methane in outer planet atmospheres.

The revised methane band model parameters and fitted k-coefficient tables described in this paper are freely available from the following web site: http://www.atm.ox.ac.uk/user/irwin/.

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