FINAL REPORT:

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I. CALIBRATION OF THE OXYGEN A-BAND FOR SAGE III

II. CALIBRATION OF WATER FOR SAGE III

III. METHANE LINE PARAMETERS AT 2.3 μm FOR MOPITT

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I. CALIBRATION OF THE OXYGEN A-BAND FOR SAGE III

In FY98-99, a laboratory study was performed to calibrate line intensities with accuracies of 2% or better, measure O_2-and N_2-broadened linewidths and their temperature dependences, and also to check accuracies of the current values of line positions and pressure-induced frequency shifts (O_2-and N_2-). This task was completed in FY99, and the revised database in HITRAN format was delivered to the **SAGE III** science team. This winter, the paper titled *EXPERIMENTAL LINE PARAMETERS OF THE OXYGEN A-BAND AT 760 nm* was published in the Journal of Molecular Spectroscopy: L. R. Brown and C. Plymate **199**, 166-179 (2000). This spring, the revised database was delivered to Dr. L. Rothman for the **HITRAN** database. In addition to changing the A-band parameters, the air- and self-broadened widths and the temperature dependence coefficients were adapted for all the oxygen transitions between 11483 and 15930 cm^{-1}.

II. CALIBRATION OF WATER FOR SAGE III

To support **SAGE III**, the line positions, intensities, air-broadened widths and pressure-induced shifts in positions for the 960 nm water transitions were measured between 9650 and 11400 cm^{-1}. Line shape coeffients at other wavelengths and quantum assignments were collected and evaluated by R. Toth at JPL. These new results were combined with existing studies of O-18 and O-17 water to form a new compilation for this spectral region. These results described in the following abstract were presented in June at the International Symposium on Molecular Spectroscopy (Session WG, paper #5) held at Ohio State University and at the **HITRAN** Database Conference (Session 5, paper #6) held at the Harvard-Smithsonian Center for Astrophysics in Cambridge, MA. At the HITRAN conference, the revised parameters were used in another talk by J. W. Brault (*The care and feeding of databases*; Session 5, paper #4) who compared synthetic spectra to the observed laboratory spectra recorded by others and reported that the new list represented considerable improvement in the database.

These results were also presented to the **SAGE III** Science team in February at the Hampton University meeting, and as a poster at the March EOS IWG in Tucson. The new list has been given to the **SAGE III** science team and to L. Rothman for **HITRAN**.

ABSTRACT: *Water Line Parameters near 0.94 μm (940 nm) for SAGE III [9650 - 11400 cm^{-1}]*

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To support the interpretation of SAGE III data and other instruments that use the water features near 940 nm, the water line parameters have been remeasured and combined with other studies to form a new composite database in HITRAN format. For this, measurements have been retrieved from fifteen laboratory spectra of pure water and nine spectra of water + air mixtures, recorded at 0.02 cm^{-1} resolution using the McMath Fourier transform spectrometer at Kitt Peak. Over 3300 line intensities and 500 air-broadened widths and 460 pressure-induced shifts in positions have been obtained at room temperature for the main isotope $H_2{}^{16}O$. These results have been combined with experimental positions and calculated intensities of $H_2{}^{18}O$ (Partridge and Schwenke 1997; Chevillard et al. 1987) and $H_2{}^{17}O$ (Camy-Peyret et al. 1999) to form a new composite database of some 5000 transitions between 9650 - 11400 cm^{-1}. This represents a total replacement for both the 1996 HITRAN water list and the correction provided by Giver et al. in this spectral interval.

Two vugraphs from these presentations:
a) demonstrate that the new intensities of strong lines are within 3% of the older measurements
b) summarize the content of the new water database.

A) RATIO OF EXPERIMENTAL LINE INTENSITIES FOR WATER at 0.96 μm

	Giver et al. 1982	Chevillard et al. 1989	Chu et al. 1993
Instrument	Grating	FTS	Dye Laser
Range (cm^{-1})	10400-10750	9500-11500	10199-10683
# lines compared with present study	56	55	13
rms of ratio	4.5 %	2.9 %	6.7 %
range of ratio	0.93 to 1.15	0.91 to 1.13	0.92 to 1.18
mean intensity ratio (other/present)	1.020	0.972	1.027

\+ Of 57 lines measured by all three studies, only one from Giver et al., two from Chevillard et al. and one from Chu et al. differed by more than 15% from present values and were therefore omitted from consideration.

B) NEW COMPOSITE WATER DATABASE OF ~5000 TRANSITIONS

Positions and intensities from 9650 to 11400 cm^{-1}

O-16 Water ~ 3300 new measurements plus 125 weak lines from corrected HITRAN

O-18 Water Partridge/Schwenke ab initio prediction merged with Chevillard 1987:
Many positions recomputed from observed upper state levels
Some intensities rescaled (by 0.7 to 7.0) to match obs.

O-17 Water Calculated positions and intensities (Camy-Peyret et al. 1999)

Widths and shifts from 10200 to 11100 cm^{-1}

all isotopes Use 508 observed air-broadened widths
Use 462 observed pressure-induced shifts
measured temperature dependence coefficients from HITRAN

For unmeasured transitions, use "look-up" tables based on measurements in other regions:
air- broadened widths from 2.7, 1.9, 0.96, 0.82 and 0.72 µm
self-broadened widths at 6., 2.7, 1.9 and 0.72 µm ++

shifts (new work in progress by Gamache)

temperature dependence of widths (prior Remedios et al. 1990;

Grossman et al. 1989; Gamache et al. 1988)

++ Toth 2000, Toth et al. 1998; 2.7 and 1.9 _m values : work in progress R. A. Toth (JPL).

As a follow-on, R. Gamache at Univ. Mass. at Lowell was provided additional funds to calculate values based on his published air-broadening studies at 740 nm. These can be used for the 940 nm region as well to estimate air-broadening widths and shifts for which no measurements are available. He is also performing calculations of the air-broadened widths at different temperatures to predict the temperature dependence of widths of these bands. He expects these to be finished in October, 2000. These will be incorporated in time for the next **HITRAN** update for the water parameters in the visible wavelengths.

A manuscript will be submitted in October, 2000: *Empirical line parameters of $H_2{}^{16}O$ near 0.94 µm: positions, intensities and air-broadening coefficients*, L. R. BROWN and R. A. TOTH and M. DULICK.

III. METHANE LINE PARAMETERS AT 2.3 _m FOR MOPITT

To support **MOPITT**, the line positions, intensities, air-broadened and self-broadened widths and pressure-induced shifts in positions for methane transitions were measured near 2.3 µm for two **MOPITT** channels (its CO channel: 4262 - 4305 cm^{-1} and its CH_4 channel: 4352 - 4500 cm^{-1}). These measurements were done in collaboration with Benner and Devi at William and Mary College in VA and Predoi-Cross at the University of Toronto.

This region of methane has long been incompletely characterized by the line parameters on **HITRAN** (see Brown et al.). In 1996, theoretical studies at the University of Bourgogne in Dijon, France, produced a prediction of the main isotope with some 56,000 transitions involving eight vibrational states, compared to the 4600 lines of three identified bands given on **HITRAN** for this region. However, the accuracies of the calculated values were only 0.05 cm^{-1} for the line positions and 10-20% for the intensities. Unfortunately, the **MOPITT** investigators desired methane intensities with 1 to 2% accuracies and accurate line shape parameters for both self- and air-broadened methane.

The objective of the present task was therefore to improve this calculation by replacing many poorly-predicted intensities with good experimental values on a line-by-line basis. This required that some 1000 new intensities be measured to include many missing transitions. At the same time, new measurements were made to obtain the line shape parameters (widths and shifts). These new results described in the following abstract was presented in June at the HITRAN Database Conference in Cambridge, MA (Poster 20). Results were also given as a poster at the March EOS IWG in Tucson.

ABSTRACT: *$^{12}CH_4$ Line Parameters in the MOPITT channels near 2.3 µm (2300 nm)*

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Theoretical studies (by Hilico in Dijon, France) provided a prediction of some 56,000 transitions for eight $^{12}CH_4$ bands from 3400 to 4800 cm^{-1}. This greatly improved the database by adding many missing weak transitions (HITRAN 1996 had only 4632 stronger $^{12}CH_4$ features here). However, the calculated intensities were too inaccurate and the available line shape coefficients were too few in number to meet the requirements of the MOPITT experiment. The present task was thus undertaken to replace poorly calculated parameters with corresponding experimental values for lines in the MOPITT spectral intervals (its CO channel: 4262 - 4305 cm^{-1} and its CH_4 channel: 4352 - 4500 cm^{-1}). In addition, widths and pressure-induced shifts in positions were obtained for air- and self-broadened methane at room temperature. Measurements of 945 transitions were simultaneously retrieved with the multi-spectral fitting program from 7 spectra of pure $^{12}CH_4$ and 4 spectra of CH_4 + air mixtures, recorded at 0.012 cm^{-1} resolution using the McMath Fourier transform spectrometer at Kitt Peak. A new $^{12}CH_4$ **HITRAN** database was formed.

NUMBER OF NEW RETRIEVED METHANE MEASUREMENTS at 296 K

945 line positions and line intensities

778 air- broadened widths

790 self-broadened widths ‡

646 air- shifts (pressure induced shifts in position)

780 self-shifts “

‡ (*a factor of 10 more that all prior values in all spectral regions*)

A new database list was obtained by merging these new measurements with prior measurements of intensities, widths and temperature dependence of widths between 3700 and 4670 cm^{-1} (outside the **MOPITT** channel intervals), and this was given to the **MOPITT** science team last fall. This spring, some new experimental results were incorporated, and an improved linelist was distributed to the science team. The differences between the prior version and newest list involved a refinement of the line intensities:

FY99 version of the new methane database:
lines = 57330 range: 3354.8423 to 4938.0356 cm^{-1} total absorption = 8.932E-19

FY00 version of the new methane database:
lines = 57332 range: 3354.8423 to 4938.0356 cm^{-1} total absorption = 9.088E-19

Net Intensity Change = + 1.7 %

The addition of the weaker higher overtone and combination bands to the **HITRAN** compilation requires a change in the rotational quantum number format for all the methane parameters in **HITRAN**. These were discussed with L. Rothman during his May visit to JPL and is being implemented so that the new list can be included in this next update of **HITRAN**. A manuscript will be submitted in October, 2000: *Line Parameters of* $^{12}CH_4$ *near 2.3 µm for MOPITT* by A. Predoi-Cross, L. R. Brown, V. Malathy. Devi and D. Chris Benner.

David Edwards of the MOPPITT science team reports that this revised list is being used for the analysis of the MOPITT data. Calculations have been performed showing

1 ....” the spectral signals obtained assuming HITRAN'96 lines and the new line. The differences are very significant.

2. Because the new line list contains, in general, more lines, the atmospheric transmittance is reduced. This in turn reduces the TOA radiance due to solar radiation reflected by the Earth's surface.

The effect of more CH_4 lines on the MOPITT channel LMR correlation cell Average (A) and Difference (D) responses goes in opposite directions: the total A response decreases while the total D response increases.

3. In terms of percentage changes on the total signal between calculations using the new line list rather than HITRAN'96, the A signals decrease by about 0.7% while the D signals increase by about 8.3%. This is good because as the D-signal increases, so does our sensitivity to CH_4. The basic quantity used in the retrieval is the D/A ratio which, to first order, removes the dependence on surface albedo. With the new list the D/A ratio increases by about 9%. This corresponds to a large decrease in retrieved column CH_4, more than 10%. This is very significant since our measurement goal is 1%.”

The resulting database will benefit other applications as well. For example, the new methane compilation was also made available to Geoff Toon and Bhaswar Sen at JPL to help them achieve a better modeling of isotopic carbon dioxide lines in their atmospheric spectrum recorded at 0.01 cm^{-1} resolution with the *MARK IV* FTS. Previously, the incompleteness of the methane parameters precluded accurate tropospheric retrievals being obtained near 2.3 µm. However, their synthetic and observed atmospheric spectra matched so well using the new methane list that their retrieval uncertainty improved by a factor of 3. Their comparisons also revealed that additional line parameters of a different molecular species are now needed in this region; the relatively weak band of *ozone* near 4640 cm^{-1} is still strong enough to appear. In fact, this band could become a good feature for retrieving tropospheric ozone, now that the methane features are better represented.

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