GAUSSIAN QUADRATURE EXPONENTIAL SUM MODELING OF NEAR INFRARED METHANE LABORATORY SPECTRA OBTAINED AT TEMPERATURES FROM 106 TO 297 K.

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ABSTRACT

Transmission measurements made on near-infrared laboratory methane spectra have previously been fit using a Malkmus band model. The laboratory spectra were obtained in three groups at temperatures averaging 112, 188, and 295 K; band model fitting was done separately for each temperature group. These band model parameters cannot be used directly in scattering atmosphere model computations, so an exponential sum model is being developed which includes pressure and temperature fitting parameters. The goal is to obtain model parameters by least square fits at 10 cm^{-1} intervals from 3800 to 9100 cm^{-1}. These results will be useful in the interpretation of current planetary spectra and also NIMS spectra of Jupiter anticipated from the Galileo mission.

INTRODUCTION

Three sets of about 30 near-infrared spectra of methane have previously been fit using a Malkmus band model.[1] These spectra were obtained at NASA-Ames using a refrigerated White cell with path lengths from 3 to 61 meters, pressures of pure methane from several torr to several atmospheres, and temperatures clustered at 112, 188, and 295 K; at the lowest temperatures the maximum pressure used was limited to 0.5 atmosphere. An Eocom interferometer was used at 1 cm^{-1} resolution; the quartz

beam-splitter together with the InSb detector produced a useful range for these spectra from 3760 to 9200 cm^{-1}. The laboratory conditions of the spectra used in the Malkmus band model analyses are listed in Tables 1-3. The transmissions measured at the 10 cm^{-1} interval centered at 4650 cm^{-1} are also listed, along with the calculated transmissions from the Malkmus band model fit and the exponential sum fit, which are described below.

At pressures sufficiently high that line profiles can be described by the Lorentz formulation, the Malkmus band model can be written in the form

$$\bar{T} = \exp\left\{-2\pi\gamma_\nu P\left[\left(\frac{k_\nu u}{\pi\gamma_\nu P}+1\right)^{1/2}-1\right]\right\}, \qquad (1)$$

where $\bar{T}$ is the mean transmission of the spectral interval centered at wavenumber ν, u is the gas abundance, and P is the pressure. Only two parameters are determined from least square fits to the laboratory spectra: the absorption coefficient k_ν, and the pressure coefficient y_ν. Our notation is similar to that used by Fink, *et al.*[2] for the Mayer-Goody band model. Some of our spectra were obtained at low pressures, making it necessary to include an approximation to the Voigt line profile in our computations of the Malkmus band model parameters. But since we adopted mean pressure broadening coefficients for methane lines at our three temperatures, there were still only two parameters, k_ν and y_ν, determined from least square fits to the spectra in each temperature group.

Methane bands are major features in the spectra of all the outer planets and the satellites Titan and Triton. Having obtained these laboratory spectra, determining parameters describing the methane spectrum that can be used in modeling the moderate resolution near-infrared spectra of these planets and satellites becomes a major goal. The Malkmus band model parameters have been extrapolated to conditions applicable for modeling Triton's spectrum, assuming a clear atmosphere.[3] But scattering processes are important in the other atmospheres, and although spectral band models have been an accepted approach for nearly 50 years,[4] the radiative transfer equation in multi-layer scattering model atmospheres cannot be solved with band model formulations of gaseous

absorption. Additionally, the Malkmus band model parameters were determined only at three specific temperatures; a representation of the temperature dependence at each interval is also needed for atmospheric modeling computations.

For applications in scattering atmospheres, it is preferred that the gaseous absorption be expressed as a weighted sum of exponentials. For example, McKay, *et al.*[5] used the following expression to transform the room temperature Mayer-Goody band model parameters of Benner and Fink[6] into exponential sum parameters at intervals of about 500 cm^{-1} for use in Titan greenhouse model computations:

$$\bar{T} = \sum_{i=1}^{4} w_i \exp\left(-k_i u P^n\right) . \qquad (2)$$

Here w_i are weights, and k_i are the absorption coefficients, scaled by a pressure factor P^n, where the exponent n is a fitting parameter; this exponential sum model thus has 8 parameters to be determined from least square fits.

EXPONENTIAL SUM MODELS

In a similar fashion, Tomasko, *et al.*[7] made some preliminary transformations of the Malkmus band model parameterization of the Ames spectra for use in modeling certain intervals of the Titan spectrum of Fink and Larson.[8] For computational efficiency in the scattering model atmosphere, Tomasko preferred an 8 term exponential sum using fixed Gaussian quadrature weights. Despite the higher number of terms, this model has about the same number of parameters to determine as the 4 terms used by McKay, et al., since the weights are fixed: $w_1 = w_8 = 0.0506$, $w_2 = w_7 = 0.1112$, $w_3 = w_6 = 0.1569$, and $w_4 = w_5 = 0.1813$. In this model the absorption coefficients are required to increase in order with the term number, i.

Instead of determining exponential sum parameters from transmission values computed from band model fits, a more direct approach should be to determine the exponential sum parameters directly from the measured transmission values of the laboratory

spectra. Pressure and temperature parameters should be included; with the large number of parameters, better fits should be obtained than from 2 parameter band models. The exponential sum model should have the following form:

$$\bar{T} = \sum_{i=1}^{8} w_i \exp\left[-k_i u f_1(P) f_2(T)\right], \qquad (3)$$

where u is the methane abundance, $f_1(P)$ is a function of pressure, and $f_2(T)$ is a function of temperature.

This expression requires that a number of decisions be made before final results can be determined by least square fits. Since a P^n dependence is not realistic at very low pressures, we introduced a second pressure parameter, P':

$$f_1(P) = \left(P + P'\right)^n . \qquad (4)$$

Since the spectra were obtained in three temperature groups, we initially selected a 2 parameter temperature dependence:

$$f_2(T) = \exp\left[a\left(\ln T/T_o\right)^2 + b \ln T/T_o\right], \qquad (5)$$

where $T_o = 273$ K, and a and b are fitting parameters. An additional term-dependent temperature parameter, c, was introduced when it was realized this would permit better fits in the lower temperature groups:

$$\bar{T} = \sum_{i=1}^{8} w_i \exp\left(-k_i \left\{1 + \left[(1+c)^{i-4} - 1\right] \ln \frac{T}{T_o}\right\} u f_1(P) f_2(T)\right). \qquad (6)$$

PRELIMINARY RESULTS

The exponential sum model in equation (6) above has 13 fitting parameters; the Ames transmission measurements of the 10 cm^{-1} spectral interval centered at 4650 cm^{-1}

was fit quite well by this model. Comparisons of the observed transmissions, the exponential sum model computations, and the Malkmus band model computations are presented in Tables 1-3. This spectral interval has both a substantial pressure dependence and temperature dependence; being high in the R branch of the $\nu_2 + \nu_3$ band, the absorption decreases dramatically at low temperatures.

The fitting parameters for equation (6) determined at 4650 cm^{-1} are: k_1=0.0227, k_2=0.0319, k_3=0.0415, k_4=0.0501, k_5=0.1173, k_6=0.4775, k_7=1.159, k_8=17.0, a=-0.845, b=0.472, c=0.085, P'=0.0383 atm., and n=0.615.

DISCUSSION

Several problems must be overcome before determining exponential sum model parameters at all the spectral intervals where Malkmus band modeling was done. The forms of the pressure and temperature functions must be chosen which can adequately represent the transmission data at all spectral intervals. Spectra were obtained at pressures from several Torr to several atmospheres; the 2 pressure parameters P' and n of equation (4) may be insufficient to fit the data well at all intervals. Similarly, a temperature dependence may be found to improve equation (5). We have made a few tests to see if fits could be improved by allowing the pressure exponent, n, to vary with the term index, i, in equation (6). Fits were significantly improved, but more fitting parameters increase the risk of coupling between parameters, raising concerns about the uniqueness of the fits, and significantly increasing computation time.

Even to get unique values for all 8 absorption coefficients, transmission values must range from over 0.95 to less than 0.05. This requirement was readily met by the Ames spectra at 4650 cm^{-1}, as shown in Tables 1-3, but certainly not at all spectral intervals. In regions of strong absorption, it will be useful to combine the Ames room temperature spectra with some of the room temperature spectra obtained by Benner and Fink[6] at the Lunar and Planetary Laboratory. The conditions of some of these spectra are listed in Table 4. Since the abundance and pressure conditions of some of

Table 1.

Ames Room Temperature Spectra

Spectrum Number	Methane Abund. m-amgts.	Pressure atm.	Temp. Kelvin	Transmission at 4650 cm^{-1} measured	Malkmus model	Exp. Sum model
A002	0.2825	0.0971	296	0.946	0.952	0.939
A003	0.7274	0.2500	296	0.875	0.888	0.871
A004	1.66	0.5697	296	0.747	0.767	0.738
A005	4.048	1.3878	296	0.520	0.527	0.513
A006	8.806	3.0070	296	0.260	0.249	0.262
A007	19.53	6.6260	295	0.043	0.046	0.043
A012	1.145	0.1003	295	0.867	0.879	0.871
A013	2.854	0.2500	295	0.725	0.741	0.727
A014	6.498	0.5684	295	0.497	0.513	0.522
A015	16.04	1.4010	295	0.228	0.195	0.232
A016	34.55	3.0070	295	0.039	0.030	0.035
A017	76.87	6.6460	295	0.000	0.000	0.000
A026	0.295	0.0052	295	0.960	0.962	0.961
A027	0.817	0.0144	295	0.930	0.929	0.920
A028	2.243	0.0395	295	0.849	0.862	0.847
A029	5.672	0.1000	295	0.704	0.724	0.693
A030	14.19	0.2500	295	0.462	0.466	0.464
A034	32.35	0.5697	295	0.202	0.179	0.196
A036	170.9	2.9930	295	-0.003	0.000	0.000
A041	2.558	0.1000	295	0.795	0.812	0.799
A042	6.399	0.2501	296	0.609	0.614	0.602
A043	14.59	0.5699	296	0.369	0.336	0.366
A044	35.76	1.3950	295	0.092	0.070	0.084
A054	0.5775	0.1004	295	0.911	0.921	0.909
A055	1.438	0.2499	295	0.801	0.825	0.812
A056	3.276	0.5696	295	0.637	0.652	0.637
A057	8.081	1.4010	295	0.378	0.351	0.379
A058	17.33	2.9930	295	0.124	0.107	0.126
A059	44.7	7.6600	295	0.001	0.003	0.002

Table 2.

Ames Methane Spectra near T=188 K.

Spectrum Number	Methane Abund. m-amgts.	Pressure atm.	Temp. Kelvin	Transmission at 4650 cm^{-1} measured	Malkmus model	Exp. Sum model
A063	0.293	0.0637	187	0.965	0.968	0.966
A064	0.767	0.1725	194	0.920	0.923	0.910
A065	1.705	0.3771	191	0.822	0.839	0.827
A066	4.257	0.9296	189	0.634	0.647	0.630
A067	9.518	2.0610	189	0.387	0.379	0.389
A068	61.47	12.2450	187	0.000	0.002	0.001
A069	24.44	5.1770	189	0.073	0.084	0.081
A072	0.59	0.0646	186	0.938	0.950	0.943
A073	1.479	0.1620	186	0.869	0.884	0.879
A074	3.467	0.3791	186	0.732	0.750	0.747
A078	19.22	2.0880	187	0.222	0.206	0.235
A081	1.147	0.0647	190	0.908	0.925	0.913
A082	2.87	0.1609	189	0.808	0.828	0.822
A083	6.803	0.3788	188	0.623	0.642	0.640
A084	16.81	0.9276	187	0.368	0.337	0.373
A087	38.93	2.1429	188	0.084	0.080	0.093
A090	2.666	0.0650	184	0.863	0.879	0.868
A091	6.605	0.1636	187	0.708	0.732	0.717
A092	15.24	0.3828	190	0.489	0.486	0.492
A093	37.07	0.9378	192	0.200	0.172	0.189
A096	84.92	2.0880	188	0.019	0.019	0.015
A099	0.302	0.0642	183	0.962	0.968	0.966
A100	0.765	0.1633	184	0.916	0.924	0.916
A101	1.782	0.3818	185	0.822	0.834	0.828
A102	4.346	0.9330	186	0.640	0.643	0.631
A105	9.619	2.0820	189	0.396	0.376	0.385
A108	0.311	0.0036	191	0.965	0.979	0.976
A109	0.842	0.0096	191	0.952	0.961	0.945
A110	2.306	0.0263	191	0.912	0.917	0.892
A111	5.674	0.0647	191	0.806	0.822	0.790
A112	14.38	0.1622	189	0.591	0.616	0.587
A115	26.47	0.3726	189	0.405	0.376	0.385
A116	66.58	0.9342	189	0.081	0.086	0.086
A120	192.8	2.6780	190	0.000	0.001	0.000

Table 3.

Ames Methane Spectra near T=112 K.

Spectrum Number	Methane Abund. m-amgts.	Pressure atm.	Temp. Kelvin	Transmission at 4650 cm^{-1} measured	Malkmus model	Exp. Sum model
A123	0.1295	0.0020	115	0.993	0.996	0.997
A124	0.3652	0.0054	112	0.989	0.990	0.993
A125	1.009	0.0146	109	0.978	0.977	0.982
A126	2.575	0.0382	112	0.945	0.946	0.947
A127	6.27	0.0931	112	0.875	0.878	0.881
A128	14.21	0.2109	112	0.728	0.745	0.754
A129	35.08	0.5208	112	0.477	0.486	0.496
A132	0.0608	0.0020	113	0.999	0.998	0.999
A133	0.1626	0.0053	I09	0.997	0.994	0.997
A134	0.464	0.0147	107	0.989	0.986	0.992
A135	1.179	0.0371	106	0.979	0.968	0.977
A136	3.612	0.1147	107	0.924	0.909	0.919
A137	7.36	0.2338	107	0.846	0.825	0.843
A138	15.34	0.5237	115	0.663	0.666	0.646
A141	0.295	0.0020	112	0.984	0.992	0.995
A142	0.799	0.0054	113	0.980	0.983	0.985
A143	2.183	0.0150	115	0.954	0.962	0.958
A144	5.41	0.0369	114	0.906	0.916	0.908
A145	13.73	0.0929	113	0.793	0.806	0.807
A146	31.27	0.2112	113	0.618	0.615	0.615
A147	77.68	0.5250	113	0.317	0.300	0.313
A150	0.0294	0.0020	114	0.993	0.999	0.999
A151	0.0823	0.0055	114	0.992	0.997	0.998
A152	0.2194	0.0147	114	0.989	0.992	0.995
A153	0.552	0.0371	114	0.978	0.982	0.985
A154	1.709	0.1158	115	0.944	0.948	0.942
A155	3.472	0.2333	114	0.895	0.897	0.887
A156	7.815	0.5204	113	0.784	0.785	0.765
A159	0.0149	0.0019	110	0.995	0.999	1.000
A160	0.0426	0.0054	109	0.998	0.998	0.999
A161	0.1164	0.0147	109	0.995	0.996	0.998
A162	0.2911	0.0368	109	0.987	0.990	0.993
A163	0.747	0.0937	108	0.972	0.974	0.978
A164	1.673	0.2117	109	0.948	0.944	0.939
A165	4.015	0.5314	114	0.870	0.869	0.839

Table 4.

L.P.L. Methane Spectra

Spectrum Number	Methane Abund. m-amgts.	Pressure atm.	Temp. Kelvin
170A	0.856	0.905	294
170C	0.851	0.901	294
140A	0.477	0.505	294
120A	0.260	0.275	294
120C	0.260	0.275	294
110A	0.129	0.137	294
105A	0.0653	0.0691	294
102A	0.0255	0.0270	294
H70A	0.439	0.911	294
H40A	0.254	0.528	294
H40C	0.254	0.528	294
H20A	0.125	0.259	294
H10A	0.0609	0.126	294
H05A	0.0322	0.0668	294
Q70A	0.224	0.922	294
Q40A	0.129	0.528	294
Q20A	0.0641	0.263	294
Q10A	0.0317	0.130	294
Q05A	0.0163	0.0671	294
M11A	0.590	0.0083	297
M12A	1.06	0.0150	297
M13A	1.99	0.0280	297
M15A	9.57	0.1347	297
M21A	1.18	0.0083	297
M22A	2.13	0.0150	297
M23A	3.98	0.0280	297
M31A	2.35	0.0083	297
M32A	4.26	0.0150	297
M33A	7.96	0.0280	297
M41A	4.71	0.0083	297
M42A	8.52	0.0150	297
M51A	9.42	0.0083	297

these spectra are quite different from the spectra listed in Table 1, combining these 2 sets in exponential sum modeling will increase the number of regions where good fits can be determined directly from the transmission data.

In the weak absorption regions between the main bands, the number of parameters that can be determined directly from the transmission measurements on the spectra will be greatly reduced. Nevertheless, some of these weak absorption regions are of primary interest in the spectra of the outer planets and Titan, and exponential sum model parameters are needed. Our original expectation was that exponential sum parameters could best be determined from the measured transmissions, as compared to computed transmissions based on band model parameters.[7] In regions of strong absorption with sufficient lab data, this approach should give the best results. But in the weak absorption regions it will be necessary to augment the measured transmissions with computed transmissions based on the Malkmus model parameters in order to determine complete sets of exponential sum parameters. Such a procedure could become quite arbitrary unless it is closely coupled to intended applications. At this time methane exponential sum parameters are needed for modeling Titan's spectrum, and thus improving knowledge of Titan's haze, cloud elevations, and methane abundance. In six years Galileo will be in orbit around Jupiter, and the NIMS instrument should be producing many interesting spectra, requiring intensive modeling of various regions of the Jovian atmosphere.

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