$^{14}CO_2$ LASER HETERODYNE MEASUREMENTS OF FREQUENCIES AND INTENSITIES OF ETHANE NEAR 12 MICRONS

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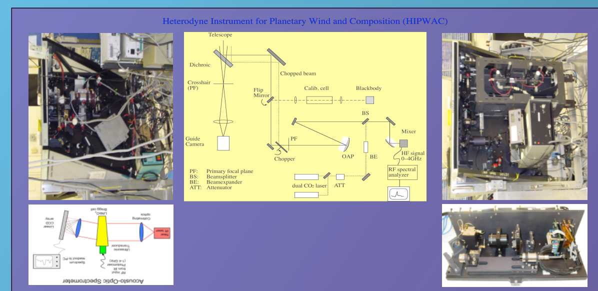
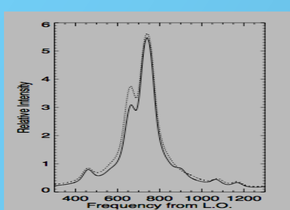
The UT/GSFC molecular line atlas for the ν_9-band of normal-isotope ethane, based on Fourier transform spectroscopy, was included in HITRAN distributions in the 1980's. The accuracy of the transition frequencies has been verified in laboratory infrared heterodyne spectroscopy to better than 0.00015 cm^{-1} (~4.5 MHz). The HITRAN distribution currently includes an atlas by Vander Auwera et al., which generally agrees with the older UT/GSFC atlas. Vander Auwera et al. have also have included the $\nu_9 + \nu_4 - \nu_4$ hot band, which is significant in the measured 12 μm spectrum. Recent laboratory measurements of ethane using infrared heterodyne spectroscopy with a resolution of 0.00003 cm^{-1}(1 MHz) confirms the Vander Auwera et al. atlas as an improvement over the older UT/GSFC atlas, and have discovered a series of previously unidentified lines not present in either atlas.

Analysis and interpretation of ethane spectra near 12 μm from the stratospheres of the outer planets and Titan measured from spacecraft (*Voyager IRIS*, *Cassini CIRS*) and from ground based observatories has always been limited by the available accuracy of ethane molecular parameters. Accuracy in the retrieval of abundance distributions and temperature structure in the planetary atmospheres observed is dependent on the knowledge of the absolute band and line intensities in the spectrum measured. The absolute infrared intensities of transitions in the band of ethane have long been a subject of controversy. Until recently, available line atlases (HITRAN, GEISA, U. Tennessee/Goddard) did not provide adequate parameter accuracy to properly analyze the high quality remote spectral data available today. Recent laboratory measurements yield ethane line intensities with uncertainties to better than 5% and line frequencies to better than 0.0001cm^{-1}.

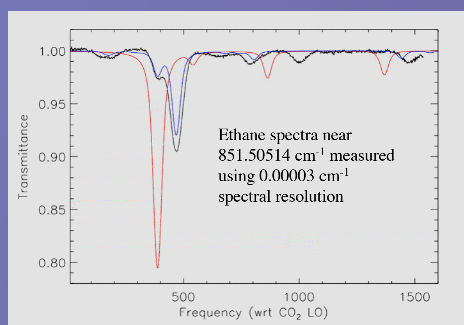


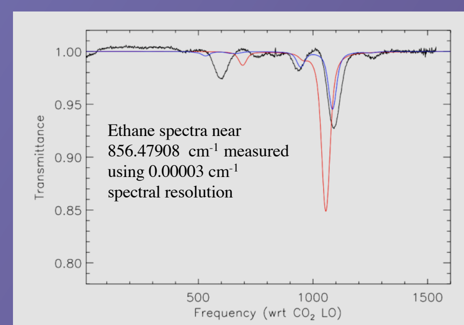


Modeled ethane spectra from Titan as observed in 2003 using the old (dotted) Tennessee/Goddard atlas and new (solid) Tennessee/Goddard atlas reported here. Note the difference in the relative intensity of the weak to strong line with consequences for the interpretation of such spectral observations.

laser line	Assignment ΔKΔJ,K,J,σ	OBSERVED (cm^-1)	OBS-ATL mcm-1	OBS-ATL MHz	OBS-L2 mcm-1	OBS-L2 MHz	MEAS INT cm/mol	ATLAS INT TN/G1983	ATLAS TN/G2007	L2 INTEN cm/mol	L3 INTEN cm/mol
P10		858.1583905									
	RR(6,14,0)	858.1101064	0.14644	4.3888096	0.04644	1.392228	5.937E-22	5.152E-22	5.94E-22	6.4E-22	6.78E-22
	RR(6,14,2)	858.1064292	-0.08077	-2.4206917	0.08923	2.675011	3.001E-22	2.634E-22	2.97E-22	3.2E-22	3.39E-22
P12		856.515448									
	RR(4,17,2)	856.4790288	-0.20125	-6.0313139	-0.02125	-0.63691	4.715E-22	4.158E-22	4.77E-22	5.14E-22	5.44E-22
P16		853.180996									
	RR(7,8,1)	853.1212927	0.072657	2.177526	0.102657	3.07755	8.019E-22	6.963E-22	8.08E-22	8.62E-22	9.13E-22
P18		851.489499									
	RR(5,11,1)	851.5051619	0.071949	2.1563139	0.131949	3.955701	6.834E-22	6.114E-22	7.08E-22	7.54E-22	7.99E-22
P22		848.0579728									
	PR(2,23,0)	848.0974171	-0.58291	-17.469878	0.287088	8.606606	5.36E-23	5.537E-23	5.17E-23	5.57E-23	5.89E-23
	PR(3,25,3)	848.0037379	0.097947	2.9354606	-0.12205	-3.65904	1.51E-22	1.315E-22	1.42E-22	1.53E-22	1.62E-22
P24		846.3179398									
	RQ(9,20,3)	846.3246914	-0.05858	-1.7555186	0.331424	9.935764	2.114E-22	1.86E-22	2.06E-22	2.2E-22	2.33E-22
P30		841.0006684									
	RQ(7,15,1)	840.9943093	-0.17069	-5.1154567	0.099314	2.977337	3.81E-22	3.267E-22	3.72E-22	3.92E-22	4.16E-22
P32		839.1958112									
	PR(2,16,2)	839.2303144	-0.10556	-3.1635469	-0.38556	-11.5586	3.254E-22	2.888E-22	3.27E-22	3.44E-22	3.64E-22
	PR(4,20,2)	839.1480996	-0.11043	-3.3097046	-0.02043	-0.61250	1.896E-22	1.675E-22	1.84E-22	1.95E-22	2.06E-22

Results for the best 11 measured ethane absorption lines compared to the Tennessee/Goddard atlas (Atakan, 1983) and Auwera et al. (2007)

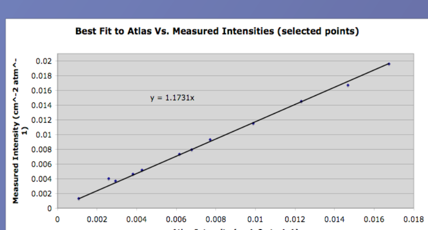


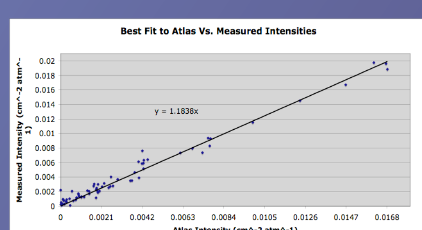


HIPWAC utilizes the infrared heterodyne technique, in which an infrared source (black body emission transmitted through the gas filled sample cell) is combined with a laser local oscillator and focused on a photomixer, where the difference frequency between the source and laser is retrieved and analyzed. The difference frequency is in the RF region of the spectrum and it preserves the intensity and infrared frequency information. Using these techniques HIPWAC is able to achieve a very high spectral resolution ($\lambda/\Delta\lambda > 10^6$) and a high frequency specificity ($>10^{-8}$) in order to study low-pressure gases. The RF spectra were retrieved using an Acoustic-Optical Spectrometer (AOS) with a sampling interval of 1 MHz. This resolution permits retrieval of true line profiles of individual ethane transitions at pressures well below 1 Torr. Absolute frequency measurements were made relative to $^{14}C^{16}O_2$ laser lines (P(10) at 858.1583905 cm^{-1} to P(32) at 839.1958112 cm^{-1}) whose line transitions are known to ~10^{-12}. The detector/photomixer is a liquid helium cooled HgCdTe photodiode. The ethane used to fill the sample cell was a research grade (99.96%) obtained from Matheson Gas Products. The gas was contained in a 30 cm straight-path cell with ZnSe windows. The gas pressure was 0.709 Torr, as measured by a 1 Torr MKS Baratron gauge, at a temperature of 26°C. Additional measurements were also done at 1.4 Torr and 2.8 Torr. The spectra acquired were fitted using an IDL radiative transfer program (Hewagama *et al.* paper in this Workshop). The quantum assignments were identified using previous atlases (Tennessee/GSFC and GEISA).

LEGEND

----- HITRAN
----- Univ. TN Atlas
----- AOS





	TN/G Atlas Correction
All Lines	1.1838
Limited Sigma	1.1799
No Low Amplitude	1.1799
Best Single Lines	1.1731
Bi-weight Regression	1.1841
Mean	**1.18012**
Standard Deviation	0.004379022

Sixty-six transitions were identified and frequencies and intensities were measured. These intensities were used to obtain a correction factor to the Tennessee/Goddard atlas by carrying out a linear fit of the atlas intensities to the measured intensities of 21 transitions that were judged to be good representatives of high quality intensity observations. The data were analyzed using a modified version of the iterative, modified bi-weighting, stepwise regression system used in Lin et al. (1980) and Daunt et al. (1984). Termination of the bi-weighting iterations was controlled by an expected-variance-driven Komolgrov-Smirnov (K-S) test Press et al. (1986). When a maximum probability, that the residuals of the non-zero weighted observations are drawn from a normal distribution, is achieved in the bi-weighting iterations, the process is terminated. The maximum probability in this case is 91% and the variance of the hypothetical parent distribution is generally quite close to the expected value for the experimental data. In addition, the 66 transitions and three subsets of the 66 were analyzed with a zero intercept linear regression program. The subsets were (a) higher amplitude lines less subject to baseline problems, (b) lines with reasonable half-widths, and (c) a selection of the best single transitions. Table above shows the multiplicative factor for each of the 5 selections of lines. The mean correction factor is taken to be the best estimate.