New results on formaldehyde, formic acid and nitric acid

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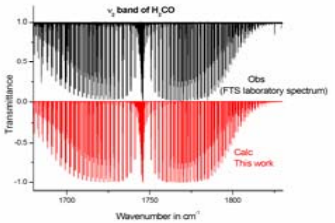
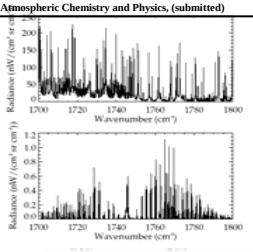
Formaldehyde H_2CO

Formaldehyde (H_2CO) is detected in the troposphere in the 3.5 and 5.7-µm regions. It is thus necessary to have a very accurate description of H_2CO absorbance in terms of individual line positions and line intensities. A linelist of the 3.5 µm region was implemented several years ago in the HITRAN and GEISA databases, which is highly deficient. For the 5.7 µm region, there is no parameters in GEISA or HITRAN. Two recent studies (Perrin 2003, Perrin 2006) try to guess with these problems. One of the remaining problem is for getting « absolute » line intensities at 3.5 and 5.7-µm.

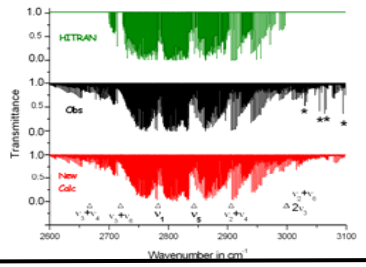
The 5.7 µm region (the ν_2 band)

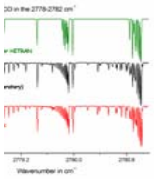


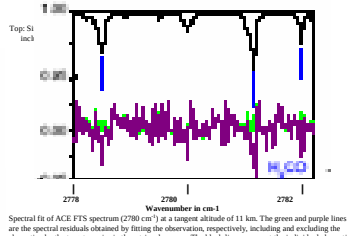
Retrieval of formaldehyde from high-resolution MIPAS-Envisat spectra
T. Steck, N. Glatthor, T. von Clarmann, H. Fischer, J. M. Flaud, B. Funke, U. Grabowski, M. Höpfner, S. Kellmann, A. Linden, A. Perrin, and G. P. Stiller
Atmospheric Chemistry and Physics, (submitted)



The 3.6 µm region (the ν_1 and ν_5 bands)







Spectral fit of ACE FTS spectrum (2780 cm^{-1}) at a tangent altitude of 11 km. The green and purple lines are the spectral residuals obtained by fitting the observation, respectively, including and excluding the absorption by the target species in the retrieval process. The black lines represent the individual absorption contribution of the H_2CO and the vertical blue lines indicate the position of the principal spectral features.
From « ACE-FTS observation of a young biomass burning plume: first reported measurements of …H2CO..by infrared occultation from space P.-F. Coheur, H. Herbin, C. Clerbaux, D. Hurtmans, C. Wespes, M. Carleer, S. Turquety, C. P. Rinsland, J. Remedios, D. Haughstaine, C. D. Boone, and P. F. Bernath, Atmos. Chem. Phys., 7, 5437–5446, 2007 »

Band intensities : intercomparison between the two spectral regions

Band intensity #		HITRAN or GEISA (line by line)	Sharpe 2004 (cross sections)	This work (line by line)
S_2	1660-1820 cm^{-1}	No data	1.284(64) #	1.161(8) #
(S_1 & S_3)	2600-3100 cm-1	2.162#	2.847(142) #	2.756(14) #
Ratio:				
(S_1 & S_3)/S_2			2.217(221)	2.374(28)

(in 10^{-17} cm^{-1}/(molecule.cm^{-2}))

#Band intensities in 10^{-17} cm^{-1}/(molecule.cm^{-2})

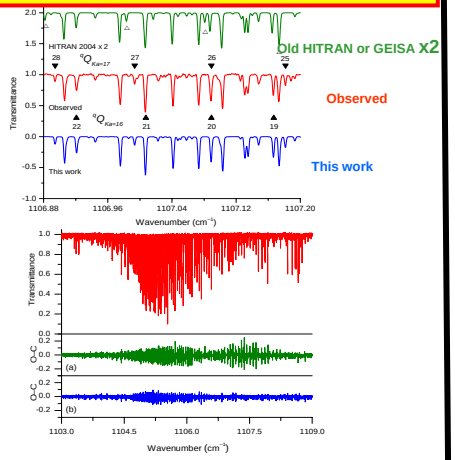
Conclusions for the H_2CO line parameters in GEISA or HITRAN:
There is no data at 5.7 µm
At 3.6 µm the linelist is of poor quality and the overall intensities are under estimated by 20%

[] S. W. Sharpe et al., *Applied Spectrosc.*, 58 (2004) 1452.,
[] http://ether.ipsl.jussieu.fr/ether/,
[] - Jacquinet-Husson N., et al., The 2003 edition of the GEISA/IASI spectroscopic database, *JQSRT*. 95, 429-467, (2005).
[] http://cfa-www.harvard.edu/HITRAN/ & L. R. Brown et al., *J. Mol. Spectrosc.*, 75 (1979) 406.
[] A. Perrin et al., *J. Mol. Spectrosc.*, 221 (2003) 192.
[] A. Perrin et al., *J. Mol. Spectrosc.*, 780 (2006) 28.

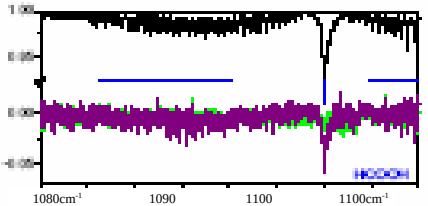
Formic acid HCOOH

Carboxylic acids such as formic acid are ubiquitous chemical constituents in the troposphere. The analyses of atmospheric spectra and retrievals of HCOOH abundances have relied on the observation of the sharp *Q*-branch structure of the strong ν_6 band located at 1105 cm^{-1} and the use of line parameters available in databases, such as GEISA or HITRAN. The previous line parameters for the ν_6 band of formic acid in HITRAN and GEISA (until 2006) were generated using incorrect line intensity parameters for the ν_6 band of HCOOH (for this list, the sum of line intensities is equal to **17.57 cm^{-2}.atm^{-1}** at 296 K). The present work lead to an improvement of the parameters for the ν_6 band of trans-HCOOH, as well as the ν_8 interacting band near 1033.47 cm^{-1}. We first measured absolute line intensities in these bands using high-resolution Fourier transform spectroscopy. Then, we generated a new set of line parameters for the 9 mm region and showed that it provides a significantly improved modeling of that spectral region. These new parameters, which lead to a band intensity of **35.1 cm^{-2}atm^{-1}** are now in GEISA and HITRAN.

[] Vander Auwera J.,K. Didriche, A. Perrin and F. Keller, "Quantitative spectroscopy in formic acid: Absolute line intensities in the v6 and v8 infrared bands of the monomer and dissociation constant of the dimmer" , *J. Chem. Phys.* 126, 124311- 1-9 (2007)
[] A.Perrin, J. Vander Auwera, "An improved database for the 9µm region of the formic acid", *JQSRT*, 108, 363, (2007)

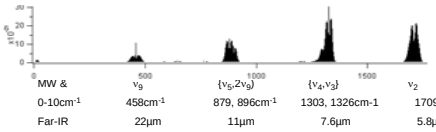


	GEISA	HITRAN	This work
Band(s)	ν_6	ν_6	ν_6 / ν_8
ν_{min}	1060.96	959.81	940.20
ν_{max}	1161.25	1234.68	1244.41
Σ S	17.57 cm^{-2}atm^{-1}	17.51 cm^{-2}atm^{-1}	35.1 cm^{-2}atm^{-1}
S_{ij}^a	2.4	2.0	4.0
No. of lines	3388	18000	49625

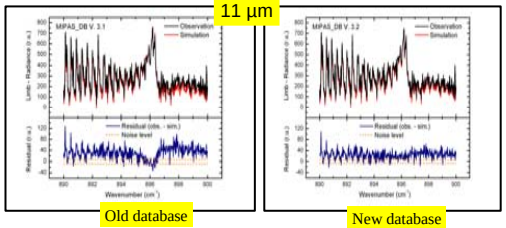


Spectral fits of the spectrum at a tangent altitude of 11 km in the 1100 cm^{-1} region (Q branch of the ν_6 band of **HCOOH**) is observed. The green and purple lines are the spectral residuals obtained by fitting the observation, respectively, including and excluding the absorption by HCOOH in the retrieval process. The black lines represent the individual absorption contribution of the molecule and the vertical blue lines indicate the position of the principal spectral features. **From « ACE-FTS observation of a young biomass burning plume: first reported measurements of …HCO..by infrared occultation from space P.-F. Coheur, H. Herbin, C. Clerbaux, D. Hurtmans, C. Wespes, M. Carleer, S. Turquety, C. P. Rinsland, J. Remedios, D. Haughstaine, C. D. Boone, and P. F. Bernath,** Atmos. Chem. Phys., 7, 5437–5446, 2007 »

Nitric acid (HNO_3)



11 µm

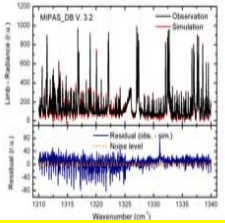


Comparison of observed and simulated MIPAS spectra in band A
for an altitude of 24km

Flaud J.-M., G. Brizzi, M. Carlotti, A. Perrin and M. Ridolfi
Atmos. Chem. Phys., *6*, 1–12, 2006.

ν_3 band, Q branch

Status of the ν_3 & ν_4 bands (7.5µm)
…still unsatisfactory !!!!!!!!



Work in progress, using new FTS data and a new model