CH3CHO PSEUDO-LINELIST

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INTRODUCTION.

This document gives information on the pseudo-linelist for Acetaldehyde (CH3CHO) derived at JPL in November 2005.
The linelist was created based on three data sets of absorption cross-sections from laboratory measurements taken at the Pacific Northwest National Laboratory (PNNL) by Steven Sharpe and co-workers, and two absorption spectra taken at the California Institute of Technology (CIT) by Paul Wennberg and co-workers.
The PNNL data consists of pressure broadened measurements at three different temperatures and moderate resolution. The CIT data is available only at room temperature but with high resolution in both a pressure broadened and a non-pressure broadened case. The characteristic quantities for the different measurement sets are given in the following table.

#	Source	Temp.	p_ch3cho	p_tot	Freq.-range	Res.	Spacing	l_cell
1	PNNL	323	2.2	760	510-6500	0.1125	0.060	19.96
2	PNNL	298	2.2	760	510-6500	0.1125	0.060	19.96
3	PNNL	278	2.2	760	510-6500	0.1125	0.060	19.96
4	CIT	293	10.7	10.7	2500-3500	0.008	0.004	10.30
5	CIT	293	10.7	513	2500-3500	0.008	0.004	10.30

Temp. - Temperature in K
p_ch3cho - CH3CHO partial pressure in torr (assumed for PNNL)
P_tot - Total pressure in torr
Freq.-range - Frequency range in cm-1
Res. - Resolution in cm-1
Spacing - Spectral point spacing in cm-1
l_cell - Cell length in cm

DESCRIPTION.

The PNNL cross-sections were converted back into transmittance spectra using the cell length and an average gas concentration.
The CIT spectra were ratioed using an empty cell spectrum taken in the same set-up as the absorption spectra. All resulting laboratory transmittance spectra were then simultaneously fitted (using the GFIT algorithm) in appropriate frequency bands by iteratively adjusting the strengths and ground-state energies of the pseudo-lines.

Due to the different frequency coverage and resolution of the PNNL and CIT spectra, different pseudo-line spacings were used for fitting different frequency bands. In a region between 1000 and 1900 cm-1, where only PNNL spectra were available, a pseudo-line spacing of 0.05 cm-1 was used.
In a region between 2600 and 2900 cm-1, where both PNNL and CIT spectra were available, a finer pseudo-line spacing of 0.005 cm-1 was used.
Fitting was performed in the regions 1000-1250 cm-1, 1250-1650 cm-1, 1650-1900 cm-1, and 2600-2900 cm-1. Because there were small residuals of water vapor and methane in the CIT spectra the water vapor and methane amounts were fitted in a narrow frequency window and taken into account during the fitting of the region at 2600-2900 cm-1. At each line frequency, an effective

strength and ground-state energy was derived by simultaneous non-linear least squares fitting to the spectra that covered the frequency band of interest. In analogy to other organics (e. g. CH3OH) an airbroadened halfwidth of 0.1 cm-1/atm and a selfbroadened halfwidth of 0.4 cm-1/atm was assumed. In the regions between 1000-1900 cm-1 both a continuum level and a continuum tilt were fitted simultaneously to the spectra, in the 2600-2900 region only a continuum level was adjusted.

The result of the fitting process is a pseudo-linelist that covers the frequency region 1000-1900 cm-1 and the region 2600-2900 cm-1, containing 78002 pseudo-lines in total. It has to be noted that at 2900 cm-1 the CH3CHO absorption is still above zero, which may result in a discontinuity if atmospheric spectra in a frequency window that reaches beyond 2900 cm-1 are fitted with the present linelist.

PARTITION FUNCTION.

The rotational partition function for acetaldehyde was assumed to be (296/T)^1.5. The vibrational partition function was calculated in the way it had been done for the ATMOS experiment, as described e. g. by Norton and Rinsland (1991). The following 15 vibrational frequencies (in cm-1) were used, all degeneracies were set to 1:

3005, 2917, 2822, 1743, 1441, 1400, 1352, 1113, 919, 509,
2967, 1420, 867, 763, 150

ACCURACY.

To estimate how well the pseudo-linelist represents the laboratory spectra, test retrievals were performed in which the laboratory spectra were fitted using the pseudo-linelist. The retrieved scale factors for the acetaldehyde abundances in the different spectra are tabulated below.

	Scale factors retrieved in freq. region			
#	1000-1250 cm-1	1250-1650 cm-1	1650-1900 cm-1	2600-2900 cm-1
1	0.9982	1.0026	1.0062	1.0360
2	1.0014	0.9945	0.9886	1.0388
3	0.9994	1.0022	1.0053	1.0588
4				0.9924
5				0.9826

In the 1000-1900 cm-1 region the pseudolines correctly represent the PNNL spectra to better than 1.5% of the given CH3CHO amount. In the region from 2600-2900 cm-1, where both PNNL and CIT spectra are available, the spectra can be fitted to better than 6%, indicating a slight inconsistency between the PNNL and the CIT measurements.

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REFERENCE.

Norton, R. H. and C. P. Rinsland, ATMOS data processing and science

analysis methods, Appl. Opt., 30, 389-400, 1991.