PAN PSEUDO-LINELIST

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INTRODUCTION.

This document gives information on the pseudo-linelist for PAN (CH3C(O)OONO2) derived at JPL in October 2005. The linelist was created based on 5 data sets of absorption cross-sections from laboratory measurements taken at the Rutherford Appleton Laboratory (RAL). The measurements and the absorption cross sections are described in Allen et al. (2005a,b).

The cross-section data sets were derived from spectra measured in regions between 550 and 2200 cm-1 at three different temperatures and pressures between 0.19 and 2.20 mbar. Each measurement used the same cell of 26.1 cm length. The resolution of the spectra was 0.25 cm-1, and they were given with a spectral point spacing of about 0.1 cm-1. The temperatures and frequency ranges for the different measurement sets are given in the following table.

#	Temp [K]	Freq.-range [cm-1]
1	295	550-1650
2	295	1650-2200
3	273	550-1400
4	250	550-1400
5	250	1600-2200

DESCRIPTION.

The cross-sections were converted back into transmittance spectra using the cell length and an average gas concentration. The resulting laboratory transmittance spectra were then simultaneously fitted (using the GFIT algorithm) by iteratively adjusting the strengths and ground-state energies of the pseudo-lines.

Due to the resolution of the laboratory spectra of 0.25 cm-1 a pseudo-line spacing of 0.1 cm-1 was chosen. Fitting was performed in the bands with centers at 794 cm-1, 1163 cm-1, 1302 cm-1, and 1741 cm-1, which correspond to the four strongest bands of PAN in the mid-infrared. Because there were still small residuals of water vapor contamination in the RAL spectra the water vapor amount was fitted in a narrow frequency window and taken into account during the fitting of the PAN bands. 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. The result of the fitting process is a pseudo-linelist that covers three frequency regions, 760-870 cm-1, 1110-1340 cm-1, and 1700-1780 cm-1. It contains 4203 pseudo-lines.

PARTITION FUNCTION.

The rotational partition function for PAN was assumed to be (296/T)^2. 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 27 vibrational frequencies (in cm-1) were used (J. Francisco, private communication), all degeneracies were set to 1:

3164, 3121, 3058, 1880, 1806, 1475, 1471, 1400, 1352, 1172, 1065,
999, 984, 828, 806, 736, 727, 616, 585, 495, 373, 327, 316, 100,
96, 82, 24

It should be noted that the derived ground-state energies are higher than for most other molecules. This is likely to be related to the large number of low-lying vibrational modes, such that very few PAN molecules are in the ground-state at the temperatures at which the spectra were measured.

ACCURACY.

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

	Scale factors retrieved in freq. region		
#	760-870 cm-1	1110-1340 cm-1	1700-1780 cm-1
1	1.0089	1.0048	
2			0.9989
3	0.9903	0.9947	
4	1.0036	1.0022	
5			1.0005

The pseudolines correctly represent the RAL spectra to better than 1% of the given PAN amount in all bands. However, it has to be noted that additional uncertainties may arise from the extrapolation of the temperature dependence of the pseudo-lines from laboratory temperatures to atmospheric temperatures. This may in particular affect the pseudo-linelist in the region from 1700-1780 cm-1 because it was created with spectra available at two different temperatures temperatures only.

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