ClNO3 PSEUDO-LINELIST

INTRODUCTION.
This documents the ClNO3 pseudo-linelist derived at JPL in November 2000 from the laboratory spectra of Manfred Birk and Georg Wagner, whose work was described at the 2000 HITRAN conference. The measurement conditions for each of these spectra are tabulated below. Each of these spectra covers the 690 to 1330 cm-1 region.

#	P_tot	P_clno3	Temp	Resn	Noise	File
1	1.068	1.0680	297.02	.0020	0.000	"missing "
2	0.558	0.5577	297.20	.0020	0.497	"297_000.xy"
3	95.08	1.0161	297.39	.0020	0.198	"297_100.xy"
4	44.76	1.0065	297.44	.0040	0.331	"297_050.xy"
5	23.91	1.0121	297.13	.0020	0.305	"297_025.xy"
6	1.013	1.0131	297.00	.00094	0.000	"missing "
7	0.321	0.3206	189.58	.0020	0.433	"190_000.xy"
8	96.24	0.6041	189.58	.0055	0.000	"missing "
9	94.59	0.3027	189.58	.0055	0.573	"190_100.xy"
10	44.96	0.3015	189.58	.0040	0.382	"190_050.xy"
11	24.57	0.3061	189.58	.0020	0.542	"190_025.xy"
12	75.73	0.3017	189.70	.0055	1.000	"190_075.xy"
13	12.74	0.2999	189.70	.0020	0.717	"190_012.xy"
14	155.8	0.3022	189.70	.0055	0.480	"190_150.xy"
15	0.603	0.6028	189.60	.00094	0.000	"missing "
16	95.42	0.6209	219.24	.0055	0.285	"219_100.xy"
17	0.303	0.3026	219.00	.0020	0.761	"219_000.xy"
18	154.2	0.3044	218.93	.0083	0.924	"219_150.xy"
19	53.40	0.3058	218.95	.0040	1.504	"219_050.xy"
20	26.10	0.3061	218.94	.0020	0.940	"219_025.xy"
21	12.83	0.3033	218.95	.0020	1.060	"219_012.xy"
22	5.225	0.3007	218.95	.0020	0.752	"219_005.xy"
23	147.8	0.3029	249.25	.0083	0.516	"249_150.xy"
24	98.30	0.6034	249.24	.0055	0.425	"249_100.xy"
25	25.59	0.3135	249.23	.0020	1.590	"249_025.xy"
26	53.53	0.6078	249.24	.0040	0.346	"249_050.xy"
27	12.72	0.3032	248.41	.0020	1.295	"249_012.xy"
28	0.303	0.3025	248.27	.0020	1.607	"249_000.xy"
29	13.86	0.3028	204.42	.0020	1.000	"204_012.xy"

P_tot is the total pressure in mbar
P_clno3 is the ClNO3 partial pressure in mbar

DESCRIPTION.
First, the cross-sections were converted back into transmittance spectra from knowledge of the cell length and gas concentrations. In transmittance, the noise will be much more constant than in absorptance, especially considering that in some of the spectra, the depth of the 780 cm-1 Q-branch is over 80%. The resulting 25 laboratory transmittance spectra were then simultaneously fitted (using the GFIT algorithm) by iteratively adjusting the strengths and ground-state energies of the pseudo-lines.

PSEUDO-LINE SPACING.
After trying various line spacings, an interval of 0.01 cm-1 was finally chosen. This difficult choice was a trade-off between:
1) minimizing the number of ClNO3 pseudo lines,

2) adequately representing the ClNO3 spectral structure,
3) getting the correct slant column abundances of ClNO3.

Having more pseudolines (e.g. 0.002 cm-1 spacing) provides better representation of the spectral structure observed in the low pressure laboratory spectra, and gives slightly more accurate representation of their slant column abundances, but the differences were small (< 1%).

But most of the atmospheric ClNO3 resides at pressures (25-75 mbar) where this fine structure is smeared by pressure-broadening. So in terms of correctly representing the ClNO3 absorption in spectra of the Earth's atmosphere, 0.01 cm-1 spacing seems to be adequate.

DISCUSSION:
Although the new laboratory ClNO3 measurements of Birk and Wagner are clearly the best to date, they are not perfect. Some minor deficiencies became apparent during the fitting of the laboratory spectra, that users of the raw cross-sections should be aware of:
1) Channel fringes of up to +/- 1% amplitude.
2) HNO3 absorptions of up to 2% depth are noticable in the 1310-1330 cm-1 region of spectrum #2 (297K; no air broadening).
3) H2O absorption lines are noticable in the 1312-1321 cm-1 region of most spectra. # 16 (219K and 95 mbar) is especially prominant; the 1318.929 cm-1 H2O line attaining 8% in depth. Note that these H2O lines are formed at room temperature and at low pressure (inside the FTIR ?), not in the cell containing the ClNO3.

To minimize propagation of these artifacts into the ClNO3 pseudo-linelist, channel fringes, H2O, and HNO3 were all fitted during the pseudo-line iteration process. Otherwise, when analyzing atmospheric spectra in the 1320 cm-1 region, H2O and HNO3 absorptions would be misidentified as ClNO3, and vice versa.

IMPLEMENTATION.
To make best use of these pseudo-lines, the assumed ClNO3 Doppler width must be approximately equal to the 0.01 cm-1 pseudo-line spacing. Otherwise the ClNO3 spectrum will start to appear "spikey" in the upper stratosphere. If your analysis software calculates the Doppler width based on the molecular weight of ClNO3, I suggest reducing it from 97 to 1.

Of course, this problem could have been completely avoided by having the ClNO3 pseudo-lines on a 0.001 grid, but then there would have been 40 Mbyte ClNO3 pseudo-linelist, rather than just 4 Mbyte.

CALCULATION OF S AND E"
At each line frequency, an effective strength and ground-state energy was derived by non-linear least squares fitting to the 25 spectra. Prior to this a PBHW of 0.078 cm-1/atm had been chosen since it gave the best overall fits to the pressure dependence of the 780 cm-1 Q-branch region. As part of the fitting, the strengths and ground-state energies were both constrained to be +ve.

After deriving the pseudo-line strengths, we noticed that in certain spectral regions (880-965, 1005-1090 and 1130-1215 cm-1) the strengths were all very small. We therefore deleted all the lines from these intervals to minimize the size of the pseudo-linelist and to save time when performing line-by-line calculations in those spectral regions.

Since the Birk laboratory spectra stop at 1330 cm-1, the new ClNO3 pseudo-linelist still contains the old pseudo-lines for the 1680-1790 cm-1 region, which were based on the measurents of Ballard et al. (1988). Note that the 1330-1340 cm-1 region, which was previously covered by Ballard's cross-section, is no longer represented in the new list.

The new ClNO3 pseudo-linelist therefore contains lines in the following 5 intervals:

V_start	V_stop	N_lines	Delta_nu	Spectra
690	- 880 cm-1	19000	0.01	Birk & Wagner
965	- 1005 cm-1	4000	0.01	Birk & Wagner
1090	- 1130 cm-1	4000	0.01	Birk & Wagner
1215	- 1330 cm-1	11500	0.01	Birk & Wagner
1680	- 1790 cm-1	1540	0.07142	Ballard et al.

Comparisons of ClNO3 retrievals from MkIV balloon spectra in the 780 cm-1 region, suggest that the new pseudo-linelist produces 5-10% smaller ClNO3 amounts than either the Bell linelist or the previous pseudo-linelist derived from the Ballard cross-sections.
Furthermore, the new cross-sections of Birk and Wagner provide much better consistency between ClNO3 amounts derived from the 780 and 1290 cm-1 regions (previously the latter gave 15% smaller amounts).
