

## AFGL atmospheric absorption line parameters compilation: 1980 version

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A new version of the AFGL atmospheric absorption line parameters compilation is now available. Major modifications since the last edition of 1978 include the updating of the strongest bands of water vapor, updated line positions for carbon dioxide, improved ozone parameters in the 5- and 10- $\mu\text{m}$  regions, and updated and additional data for methane in the 3.5- and 7.7- $\mu\text{m}$  regions. The atlas now contains over 159,000 rotational and vibration-rotation transitions from 0.3 to 17,880  $\text{cm}^{-1}$ .

There is now available a new edition of the AFGL atmospheric absorption line parameters compilation that supersedes the last public version of October 1978.<sup>1</sup> Of the seven molecular species on this main atlas, all have undergone some revisions, although the most significant modifications pertain to water vapor, carbon dioxide, ozone, and methane. The affected bands and regions of the spectrum are summarized in the following sections.

Fourteen bands of water have been studied in the latest effort (see Table I). It was known that approximately half of the line strengths of the pure rotational excited vibration band (010-010) had been overestimated.<sup>2</sup> Accordingly, the entire submillimeter spectrum of this band has been recalculated using the transformed dipole moment operator<sup>3</sup> and fourth-order perturbation theory.<sup>4,5</sup> The transition frequencies have been based on the flame spectra studies of Camy-Peyret *et al.*,<sup>6</sup> and the new positions are in good agreement with the direct observations of Kauppinen *et al.*<sup>7</sup> There is now a tenfold increase in the number of transitions that were previously tabulated since a more rigorous application of the cutoff criterion was applied to account for the effect of radiation field in the line strength calculation at low frequency. The frequency dependent cutoff is

$$C = \frac{C'\nu}{2000} \tanh \frac{c_2 \nu}{2 T_0}$$
$$= 1.5 \times 10^{-30} \nu \tanh(2.4308 \times 10^{-3} \nu),$$

where  $C' = 3 \times 10^{-27} \text{cm}^{-1}/(\text{molecule cm}^{-2})$  at 2000  $\text{cm}^{-1}$  is the standard atmospheric cutoff for water described in Ref. 8,  $\nu$  is the frequency of the line in vacuum wave numbers,  $c_2$  is the second radiation constant, and  $T_0$  is the standard temperature of the compilation, 296 K.

In the 6.3-, 2.7-, 1.9-, and 1.4- $\mu\text{m}$  regions shown in Table I, the bands have been updated by incorporating the analyses of the groups in France and at the Jet Propulsion Laboratory.<sup>6,9-19</sup> For the fundamentals, overtone, and combination bands, additional weak lines from the 1978 compilation were retained but with the frequencies updated using the differences derived from the recent listings of energy levels.<sup>6,11,12,15,18</sup> The  $\nu_1 + \nu_2$  band of  $\text{H}_2^{18}\text{O}$  (181 in the AFGL shorthand notation) and the  $4\nu_2$  band constitute data that were previously absent from the compilations. It should be remarked that recent high resolution, high temperature measurements<sup>20</sup> of water vapor in the 6.3- $\mu\text{m}$  region have shown basic agreement with the line positions currently on the compilation with the exception of high- $J$  intermediate- $K$  lines. This discrepancy (of the order of tenths of a reciprocal centimeter at high- $J$ ) would be expected from the extrapolation of the theoretical treatment of the Hamiltonian. Future work is underway to take advantage of these high temperature measurements of weak lines.

The air-broadened halfwidths generated for the bands in Table I were calculated from the theory of Davies and Oli.<sup>21</sup>

The recent availability of high resolution measurements of carbon dioxide in several regions of the spectrum,<sup>22-35</sup> as well as the discovery of some errors in the calculations of line positions on the 1978 compilation, has provided the impetus for this major update of the molecular constants and the generation of new frequencies for the AFGL data base. The updating of constants employed some 84 bands, with special em-

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Received 9 October 1980.

Table I. Modified Bands of Water for Present Compilation

$\nu_0$ (cm <sup>-1</sup> ) Band center	ISO	$\nu'$	$\nu''$	Range (cm <sup>-1</sup> )	Band sum <sup>a</sup>	No. of lines	$J_{max}$
	161	010	010	0-1029	2.225	750	19
1556.883	161	020	010	877-2439	0.8152	930	17
1594.778	161	010	000	641-2821	1038.0	1807	20
2062.306	161	100	010	1221-2616	0.0019	628	14
2161.183	161	001	010	1298-2767	0.0026	563	15
3151.630	161	020	000	2039-4402	7.537	1146	17
3657.053	161	100	000	2851-4604	48.62	1381	17
3755.930	161	001	000	2822-4517	692.5	1750	20
4666.793	161	030	000	4251-5931	0.0396	662	16
5221.24 <sup>b</sup>	181	110	000	4792-5727	0.0056	443	12
5234.977	161	110	000	4603-6005	3.716	991	16
5310.468	181	011	000	4808-5963	0.1476	734	15
5331.269	161	011	000	4609-6254	80.42	1306	18
6134.030 <sup>b</sup>	161	040	000	5904-7190	0.0018	215	12

<sup>a</sup> Sum of the line strengths on compilation given in 10<sup>-20</sup> cm<sup>-1</sup>/(molecule × cm<sup>-2</sup>).

<sup>b</sup> Bands previously absent from compilations.

Table II. Modified Bands of Ozone (666) for Present Compilation

$\nu_0$ (cm <sup>-1</sup> ) Band center	$\nu'$	$\nu''$	Range (cm <sup>-1</sup> )	Band sum <sup>a</sup>	No. of lines	$J_{max}$
1007.650	101	100	948-1036	5.53	1185	50
1015.808	002	001	958-1048	15.66	1534	55
1025.596	011	010	969-1068	40.46	1544	45
1042.084	001	000	968-1215	1260.0	3492	60
1095.329	110	010	979-1174	0.992	901	44
1103.135	100	000	967-1233	53.24	3468	60
2057.892	002	000	1945-2140	11.1	2164	54
2110.785	101	000	1968-2163	113.4	2165	55
2201.157	200	000	2059-2269	3.0	1530	55

<sup>a</sup> Sum of the line strengths on compilation given in 10<sup>-20</sup> cm<sup>-1</sup>/(molecule × cm<sup>-2</sup>).

Table III. Modified Bands of Nitrous Oxide for Present Compilation

$\nu_0$ (cm <sup>-1</sup> ) Band center	ISO	$\nu'$	$\nu''$	Range (cm <sup>-1</sup> )	Band sum <sup>a</sup>	No. of lines	$J_{max}$
571.320	446	03 <sup>1</sup> 0	02 <sup>2</sup> 0	528-616	0.248	294	50
579.364	446	02 <sup>0</sup> 0	01 <sup>1</sup> 0	527-637	5.561	195	65
580.934	446	03 <sup>1</sup> 0	02 <sup>0</sup> 0	538-623	0.657	150	50
588.768	446	01 <sup>1</sup> 0	00 <sup>0</sup> 0	523-657	98.569	240	80
588.978	446	02 <sup>2</sup> 0	01 <sup>1</sup> 0	535-649	11.118	384	65
589.168	446	03 <sup>3</sup> 0	02 <sup>2</sup> 0	546-634	0.933	297	53
1160.298	446	03 <sup>1</sup> 0	01 <sup>1</sup> 0	1114-1212	11.882	256	57
1168.132	446	02 <sup>0</sup> 0	00 <sup>0</sup> 0	1115-1228	35.193	134	67
1177.746	446	02 <sup>2</sup> 0	00 <sup>0</sup> 0	1132-1234	0.239	104	60
1246.885	448	10 <sup>0</sup> 0	00 <sup>0</sup> 0	1199-1288	1.897	112	56
1269.894	546	10 <sup>0</sup> 0	00 <sup>0</sup> 0	1215-1313	3.387	121	60
1280.356	456	10 <sup>0</sup> 0	00 <sup>0</sup> 0	1227-1323	3.270	115	57
1284.903	446	10 <sup>0</sup> 0	00 <sup>0</sup> 0	1207-1341	880.156	161	80
1291.497	446	11 <sup>1</sup> 0	01 <sup>1</sup> 0	1227-1342	99.282	341	68

<sup>a</sup> Sum of the line strengths on compilation given in 10<sup>-20</sup> cm<sup>-1</sup>/(molecule × cm<sup>-2</sup>).

phasis on the Fourier transform spectrometer measurements in the 4.3- $\mu\text{m}$  region at elevated temperature,<sup>23</sup> the FTS measurements in the 15-, 5-, and 2- $\mu\text{m}$  regions,<sup>22,30,31</sup> precise laser measurements in the vicinity of 10  $\mu\text{m}$ ,<sup>24,33-35</sup> and high resolution measurements of isotopically enriched samples.<sup>25,26,29</sup> The accuracy in line positions is generally good to a few thousandths of a reciprocal centimeter to the limits of the rotational levels reported. A more detailed discussion and the resulting molecular parameters can be found in Ref. 36. The effort has affected most of the energy levels of the main isotope (626), many of the lower levels of 636, and several of the levels of the other isotopes of interest to atmospheric transmission problems. In addition, numerous corrections to band strengths have been made to the earlier listings.<sup>37</sup>

All the line parameters in the 10- and 4.8- $\mu\text{m}$  regions for the principal isotope (666) of ozone have been recalculated.<sup>38</sup> The bands included in this present

update are summarized in Table II. The  $\nu_1 + \nu_2 - \nu_2$ ,  $2\nu_3$ , and  $2\nu_1$  bands represent data heretofore absent from the atlas. The sources for the improved positional and strength accuracies are given in Refs. 38-46. However, for the air-broadened halfwidths, an average value of 0.1  $\text{cm}^{-1}/\text{atm}$  was adopted.<sup>47,48</sup> It is hoped that future investigations will improve the situation both in regard to halfwidths and the overall parameters of the isotopes.

Although the line positions and strengths of the nitrous oxide data have been in reasonably good shape, we have made use of the recent studies conducted at the National Bureau of Standards<sup>49</sup> which had the aim of producing frequency standards in the IR for users of tunable laser devices. The updating for this latest version of the AFGL data base has been in the two regions shown in Table III. Primarily, this modification extends the accuracy of line positions, which were generally good to a few thousandths of a  $\text{cm}^{-1}$  to  $J = 40$ ,

Table IV. Carbon Monoxide Bands on AFGL Compilation

$\nu_0$ ( $\text{cm}^{-1}$ ) Band center	ISO	$\nu'$	$\nu''$	Range ( $\text{cm}^{-1}$ )	Band sum <sup>a</sup>	No. of lines	$J_{\text{max}}$
	26	0	0	4-134	1.828	35	34
	36	0	0	15-95	0.019	23 <sup>b</sup>	25
	28	0	0	27-73	0.003	14 <sup>b</sup>	19
2092.1231	28	1	0	1969-2189	1.909	61	30
2096.0674	36	1	0	1958-2201	10.52	67	33
2116.2957	27	1	0	2008-2204	0.354	53	26
2116.7912	26	2	1	2025-2194	0.057	45	22
2143.2716	26	1	0	1969-2267	981.3	79	39
4159.0272	28	2	0	4088-4216	0.014	36 <sup>b</sup>	18
4166.8198	36	2	0	4066-4235	0.078	47	23
4206.7792	27	2	0	4225-4244	0.0008	7 <sup>b</sup>	10
4260.0627	26	2	0	4109-4347	7.522	64	32
6350.4396	26	3	0	6254-6410	0.048	43	22

<sup>a</sup> Sum of the line strengths in  $10^{-20} \text{cm}^{-1}/(\text{molecule} \times \text{cm}^{-2})$ .

<sup>b</sup> Bands previously absent from compilations.

Table V. Modified Bands of Methane for Present Compilation

$\nu_0$ ( $\text{cm}^{-1}$ ) Band center	ISO	Band	Range ( $\text{cm}^{-1}$ )	Band sum <sup>a</sup>	No. of lines	$J_{\text{max}}$
1303	311	$\nu_4$	1183-1383	5.813	338	17
1311	211	$\nu_4$	1090-1544	515.1	1375	22
1533	211	$\nu_2$	1378-1764	7.200	885	19
1534 <sup>b</sup>	311	$\nu_2$	1425-1645	0.032	55	12
2596 <sup>b</sup>	311	$2\nu_4$	2462-2728	0.070	44	9
2612	211	$2\nu_4$	2385-2861	5.424	998	14
2822 <sup>b</sup>	311	$\nu_2 + \nu_4$	2656-2999	4.297	242	11
2830	211	$\nu_2 + \nu_4$	2603-3079	37.95	1770	16
2917 <sup>b</sup>	211	$\nu_1$	2765-3068	0.116	52	14
3000 <sup>b</sup>	212	$\nu_4$	2902-3146	0.887	272	
3000 <sup>b</sup>	212	$\nu_1$	2903-3071	0.054	31	
3000 <sup>b</sup>	212	$2\nu_5$	2902-3130	0.049	41	
3000 <sup>b</sup>	311	$\nu_3 + \nu_4 - \nu_4$	3034-3090	0.006	12	10
3009	311	$\nu_3$	2806-3167	29.25	409	18
3010 <sup>b</sup>	211	$\nu_2 + \nu_3 - \nu_2$	2898-3105	3.671	275	10
3010 <sup>b</sup>	211	$\nu_3 + \nu_4 - \nu_4$	2881-3136	7.280	742	14
3019	211	$\nu_3$	2810-3200	1022.0	1629	20
3062 <sup>b</sup>	211	$2\nu_2$	2930-3199	16.41	499	14

<sup>a</sup> Sum of the line strengths on compilation given in  $10^{-20} \text{cm}^{-1}/(\text{molecule} \times \text{cm}^{-2})$ .

<sup>b</sup> Bands previously absent from compilations.

to the level of rotation in the last column of Table III. Lower state energy levels have been recalculated based on the constants derived in Ref. 49. The preliminary NBS study has provided relative strengths, and these have been normalized to the strongest band of each region; the agreement has been comparable within a few percent of the strengths previously given on the compilation. Halfwidths have been based on the values provided by Toth.<sup>50</sup>

The atmospheric absorption parameters of **carbon monoxide** have been completely revised for this new edition of the compilation. Additional bands are included (see Table IV), and the cutoff has been lowered to include all lines whose strengths exceed  $10^{-24} \text{ cm}^{-1}/(\text{molecule} \times \text{cm}^{-2})$ . The improved frequencies have been attained using recently published measurements<sup>51-54</sup> to determine Dunham coefficients without having to introduce isotopic relations for the rarer isotopes. With the reporting of higher overtone intensities,<sup>55,56</sup> a more accurate dipole moment function has been obtained. This has been used together with accurate vibration-rotation matrix elements<sup>57,58</sup> to yield accurate line strengths. The line positions are expected to be accurate to  $0.001 \text{ cm}^{-1}$ . The pure rotational line strengths are accurate to better than a percent, while it is felt that the fundamentals are good to 2% and the overtone and hot band lines to ~10%.

Major revisions have been undertaken for the line parameters of **methane** at  $7.7 \mu\text{m}$  ( $\nu_4$  region) and  $3.5 \mu\text{m}$  ( $\nu_3$  region). For the former region, the list of Orton and Robiette<sup>59</sup> has been used to replace completely earlier data. However, only lines whose strengths were  $>3.3 \times 10^{-24} \text{ cm}^{-1}/(\text{molecule} \times \text{cm}^{-2})$  were retained, limiting their list which extended to  $J' = 25$  to the values of  $J'$  shown in Table V. The user of these data is referred to Ref. 59 for the discussion of sources and reliability of the parameters as well as the status of future efforts toward improving line parameters of the  $\nu_2$  and  $\nu_4$  bands. Similarly, all data of methane from 2385 to  $3200 \text{ cm}^{-1}$  have been updated on the compilation.<sup>60</sup> It will be noticed from Table V that many new bands are now included as well as the monodeuterated species (212). In addition to the bands summarized in Table V, there were 1060 unidentified lines, i.e., lines between 2430 and  $3195 \text{ cm}^{-1}$  with unassigned vibrational transition. However, over 800 of these possess lower state energies based on measurements made at different temperatures.<sup>60</sup> The remaining 254 lines were kept on the compilation with a value of  $-1$  for the lower state energy to provide a caution to users attempting to extrapolate the data base far from the standard temperature of 296 K. The reliability of the data in this region is discussed in Ref. 60.

The only modification performed for the last of the seven molecules, **oxygen**, has been to the halfwidths of the  ${}^1\Delta \leftarrow {}^3\Sigma_g$  transitions. Previously a constant value had been used, and this has been changed in favor of the rotational dependence found for the atmospheric bands by Giver *et al.*<sup>61</sup>

The atlas now contains over 159,000 transitions of the molecules water vapor, carbon dioxide, ozone, nitrous

oxide, carbon monoxide, methane, and oxygen in the  $0.3\text{--}17,880\text{-cm}^{-1}$  spectral range.

Investigations continue with an aim at improving the accuracy and completeness of the atlas for diverse applications such as the generation of synthetic spectra, retrieval of terrestrial atmospheric profiles, identification of species. A corresponding compilation of trace species is also available.<sup>62</sup> The compilation is distributed by the National Climatic Center of NOAA, Digital Product Section, Federal Building, Asheville, North Carolina 28801.

We wish to acknowledge the efforts of R. Gamache of the University of Lowell for analyses of water data. Special thanks are due to C. Camy-Peyret, J.-P. Flaud, A. Maki, G. Orton, L. Brown, and M. Esplin for making their data available prior to publication. We also wish to acknowledge helpful discussions with the late W. S. Benedict and with R. Tipping.

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