The HITRAN Atmospheric Molecular Spectroscopic Database

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The Optical Environment Division of the Air Force Geophysics Laboratory has been engaged throughout its history in the development of computer codes and databases to facilitate spectral modeling of atmospheric transmission and radiative processes. Major updates to the computer codes have recently been made available: FASCODE3 (for high resolution line-by-line calculations), LOWTRAN7 (moderate resolution band-model code), and MODTRAN (an intermediate resolution band-model code). In addition, a new edition of HITRAN, the spectroscopic molecular absorption database, has become available. HITRAN now contains greatly improved data for 30 molecular species from zero wavenumber through the visible region. There are also numerous bands of species such as the chlorofluorocarbons contained as cross-section data on the HITRAN compilation. These models and database have a significant impact on spectral simulations and remote sensing capabilities. This paper will review these recent developments and present some examples of current applications.

Introduction

Soon after the second world war, advances in the technologies of infrared detectors and the development of digital computers made it feasible to consider automated calculations of atmospheric transmittance and radiance. The U.S. Air Force at the Cambridge Research Laboratories (now the Geophysics Directorate) commenced with a long-standing program to develop codes and databases for these needs. The codes have evolved in two paths: a band model approach and a line-by-line approach. The former has given rise to the family of programs called LOWTRAN and eventually MODTRAN.

LOWTRAN7, the current edition, covers the spectral region from the microwave to the ultraviolet and provides atmospheric transmittance or radiance at a resolution of 20 cm^{-1}. It is a rapid program that has been in operation for a long time. The physics is based on a one-parameter band model and limitations are operation below 50 km and loss of small-scale spectral character.

MODTRAN is a recent code which is similar to LOWTRAN, but has an order of magnitude better resolution and uses a two-parameter band model based on pressure and temperature. The spectral and altitude ranges are similar to LOWTRAN.

FASCODE (Fast Atmospheric Signature Code) attempts to use the correct physics in a line-by-line treatment of the molecular absorption. It uses the correct line shape through the different pressure regimes of the atmosphere, and now allows for non-local thermodynamic equilibrium (thereby being valid at higher altitudes than LOWTRAN or MODTRAN). FASCODE employs clever computer methods to allow for a rapid construction of the absorption line shape and the merging of layers of the atmosphere. Nonetheless, it is slower to run than the band model codes which have built-in molecular absorption. All of these codes share basically the same algorithms for geometry, scattering, default atmospheric profiles, continua, aerosols, instrumental scanning functions, and filter functions.

Common in one way or another to all these codes is the HITRAN molecular database. HITRAN is a compilation of quantized molecular transitions from the microwave through the visible region of molecular bands that contribute to absorption or emission in the atmosphere. HITRAN must accompany the line-by-line codes as input; the band model codes now base their molecular absorption bands on HITRAN, using pre-computed bands fitted to one- or two-parameter models whose coefficients are stored with the codes. In this paper, we shall focus on the evolution of the HITRAN database.

HITRAN91 and Beyond

The original database, which appeared publicly on magnetic tape in 1973, contained information for seven infrared active gases (H_2O, CO_2, O_3, N_2O, CO, CH_4, and O_2). The spectral range at that time was from about 1 to 100 microns, and the parameters contained for each of the about 100,000 transitions were the fundamental ones required for computing transmission via the Lambert-Beers exponential law of attenuation, namely, the line position in wavenumbers (cm^{-1}), the line intensity, the lower state energy, and the air-broadened halfwidth. Since that time the database has expanded substantially. By the release of the edition of 1986 (Rothman et al. 1987), one experienced an increase in the spectral range, the number of molecular species and their isotopic variants, and in the number and accuracy of the parameters. The current edition (Rothman et al. 1992) became available in March 1991; Table 1 summarizes the species present in 1991.

In Table 1, the third column includes pure rotational and vibrationally excited pure rotational bands (in the submillimeter region), vibration-rotation bands, and some vibration-rotation bands between different electronic states (for example, oxygen). Most of the transitions are caused by electric dipole interaction with the radiation field. However, there are some electric quadrupole and magnetic dipole transitions as well (nitrogen and oxygen). The number of bands includes contributions from the different isotopic variants in the table, and no distinction is made for strength or weakness in the summary of Table 1.

The effort toward developing improved parameters is to reduce errors in remote sensing retrievals. Deficiencies in our ability to fully model transitions that are significant in long atmospheric paths, such as for ozone or some of the trace constituents, has been an enduring problem. Nevertheless, the molecular database and the transmission codes are evolving and improving. There is a periodic international convening of developers of the high resolution codes under a working group of the International Radiation Symposium (IRS) called the Intercomparison of Transmittance and Radiance Algorithms (ITRA) (IRS 1989). These meetings have gone a long way in improving codes such as FASCODE and presenting directions for the future of the codes. Similarly, there is a subgroup of the IRS called Atmospheric Spectroscopic Applications (ASA) which has concentrated on development of the database and modeling efforts such as continua, line shape, non-LTE phenomena, line-coupling effects, etc. In addition, a biennial meeting is held specifically on the molecular database at the Geophysics Directorate. The goals have been to identify deficiencies and to bring forth new improved experimental observations and theoretical calculations.

The advance of computer analytic power and the wider use of Fourier Transform Spectrometer (FTS) techniques have coupled to bring major advances to HITRAN. For example, the efforts of the group in Paris of J.-M. Flaud have made significant advances to the parameters of asymmetric rotor molecules which play a predominant role in the atmosphere.

The HITRAN'91 (Rothman et al. 1992) has substantial improvement of H_2O, CO_2, O_3, CH_4, NO_2, HNO_3, as well as refinements for most of the other species. In addition, the new species of COF_2 and SF_6 have been added, both seen in the atmosphere with strong absorption features. H_2S will be added to the next edition (particularly important because of recent volcanic activity).

Chlorofluorocarbons (CFCs) and oxides of nitrogen are examples of another direction HITRAN has taken. Because of the dense spectra for these heavier gases, it has so far been with a few exceptions, impossible to represent them in the discrete parameterized format as for the molecules represented in Table 1. The approach taken has been to use digitized high-resolution experimental data (McDaniel et al. 1991; Massie et al. 1985; Ballard et al. 1988). The latest database has many of the important bands observed at six different temperatures that span representative values for the earth's atmosphere (see Table 2). The latest generation of codes, such as FASCODE3, make use of this information and can produce quasi-quantitative simulation of atmospheric profiles. Future refinements should include representative pressures as well, in order to better model effects such as line-coupling on the band contours.

These updates have had a strong impact on remote sensing capabilities. The ozone parameters (Flaud et al. 1990) in particular have been a major improvement. An example of the improvement from the 1986 to 1991 HITRAN can be seen in Figures 1 and 2. The upper trace is a simulation using HITRAN'86 (Rothman et al. 1987); the middle trace is a simulation with HITRAN'91 (Rothman et al. 1992); and the bottom trace is the observation, a high

Table 1. Molecular Species in HITRAN

Specie	Isotopes	Number of Bands	Number of lines
H_2O	4	134	48,523
CO2	8	592	60,652
O_3	3	76	168,881
N_2O	5	140	24,125
CO	5	31	3,600
CH_4	3	48	46,971
O2	3	18	2,254
NO	3	13	7,385
SO_2	2	7	23,659
NO_2	1	8	26,296
NH_3	2	9	5,817
HNO_3	1	13	143,021
OH	3	27	8,676
HF	1	6	1,07
HCl	2	17	371
HBr	2	16	398
HI	1	9	237
ClO	2	8	6,020
OCS	4	6	737
H_2CO	3	10	2,702
HOCl	2	6	15,565
N_2	1	1	117
HCN	3	8	772
CH_3Cl	2	6	6,687
H_2O_2	1	2	5,444
C_2H_2	2	9	1258
C_2H_6	1	2	4,749
PH3	1	2	2,886
COF2	1	3	18,242
SF_6	1	1	11,520

Table 2. Cross Section Data in HITRAN

Specie	Spectral Range	Number of T	Number of pts/T
CCl_3F (CFC-11)	830 - 860	6	2 023
	1060 - 1107	6	3 168
CCl_2F_2 (CFC-12)	867 - 937	6	4 718
	1080 - 1177	6	6 539
$CClF_3$ (CFC-13)	765 - 805	6	2 696
	1065 - 1140	6	5 056
	1170 - 1235	6	4 382
$C_2Cl_3F_3$ (CFC-113)	780.5 - 995	6	430
	1005.5 - 1232	6	454
$C2Cl_2F_4$ (CFC-114)	815 - 860	6	3 034
	870 - 960	6	6 067
	1030 - 1067	6	2 494
	1095 - 1285	6	12 808
C_2ClF_5 (CFC-115)	955 - 1015	6	4 044
	1110 - 1145	6	2 360
	1167 - 1259	6	6 269
N_2O_5	555.4 - 599.8	4	93
	720.3 - 764.7	4	93
	1210.1 - 1274.8	4	135
	1680.2 - 1764.6	4	176
$ClONO_2$	740 - 840	2	10 371
	1240 - 1340	2	1 400
	1680 - 1790	2	1 540
$HN0_4$	770 - 830	1	5 476
$CHCl_2$ (CFC-21)	785 - 840	1	5 020
CCl_4	786 - 806	1	1 826
CF_4 (CFC-14)[a]	1255 - 1290	6	2 359
$CHClF_2$ (CFC-22)[a]	780 - 1335	6	11 798
HNO_3[b]	1270 - 1350	1	7 301

(a) Omitted from HITRAN'91, added to HITRAN'92
(b) Duplicated on high-resolution part of HITRAN'91

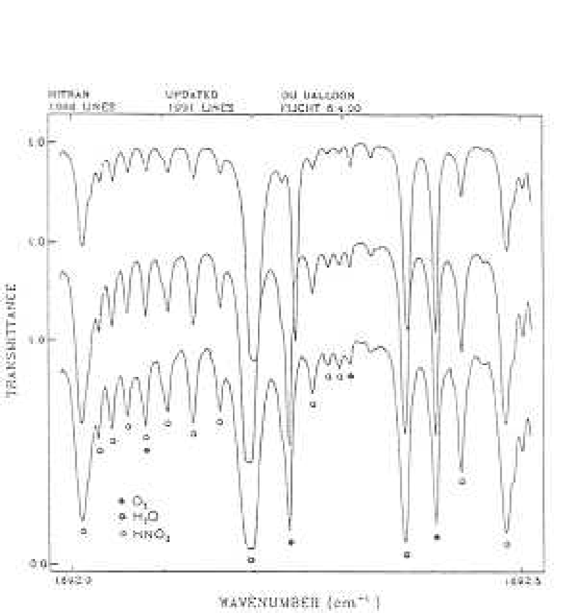

Figure 1. Simulations of University of Denver balloon-borne spectra in the 1692.0-1692.5 cm-[1] Region.

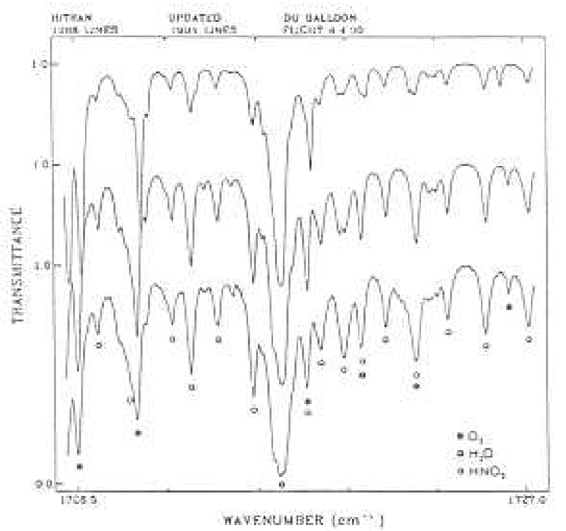

Figure 2. Simulations of University of Denver balloon-borne spectra in the 1726.5-1727.0 cm-[1] Region.

resolution balloon-borne FTS flown by the University of Denver.[a] The plots have been offset for better viewing. In these regions, the major advance is due to the improved HNO_3 parameters. For H_2O, similar results have been reported in this spectral region, and for the near infrared and visible regions.

Conclusion

HITRAN is continually evolving to better meet the requirements of a diverse group of uses: remote sensing of the atmosphere, planetary atmospheres, energetically disturbed atmospheres, combustion processes, detection of radiant sources through the intervening atmosphere, pollution monitoring, and global climate change monitoring. As new instruments in different spectral regions become operational, HITRAN endeavors to provide the parameters necessary for these tasks.

Recently, error criteria have been added to HITRAN. It is hoped that sensitivity studies will be made to better show the effects of the errors on particular simulations. The next version of the database will be available on both floppy diskettes in compressed form and optical diskettes (formerly the databases were available only on large magnetic tape). The direction is clearly for PC orientation. The user will have available more powerful tools to rapidly access subsets of data, plot data, and perform various preliminary analyses. Supplemental sets of molecular data will also be accessible. A new edition is expected in the beginning of 1992; this edition will also incorporate numerous improvements to molecular bands that were highlighted in the last HITRAN database conference.

One must emphasize that the HITRAN project is the result of the efforts of many researchers throughout the world. The megabytes of data result from the often thankless work of numerous spectroscopists analyzing, identifying, calculating, and painstakingly measuring thousands of spectral lines in laboratories and in the field.

(a) A. Goldman. University of Denver. Private Communication. 1991.

Acknowledgments

This work has been supported by the ARM program under DOE IA No. DE-AI06-90RL12076. The program has also been funded through AFOSR Task 2310G1.

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