# ARM Enhancements to HITRAN

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## Introduction

Correct radiative transfer modeling relies on the proper characterization of the molecular absorption in the atmospheric path. The knowledge of absorption parameters not only pertains to gases that are objectives of energy budget studies, but to interfering species as well. High-resolution Transmission (HITRAN) is a keystone in the simulation studies, either through line-by-line calculations [including now the infrared (IR) cross-sections] or via band-model calculations. A schematic of this interaction is shown in Figure 1. Moderate Resolution Transmittance (MODTRAN) is a band-model code where the molecular absorption has been predetermined using HITRAN with a line-by-line code, subsequently degraded to a lower resolution. The results are then fitted to a model with a limited set of coefficients that adequately describe the atmospheric profile with temperature and pressure. Fast Atmospheric Signature Code (FASCODE), FASCODE for the Environment (FASE), and line-by-line radiative transfer model (LBLRTM) are line-by-line codes that require HITRAN in real time. There is also a coupling or feedback system with laboratory measurements to provide the database with sufficient data to address deficiencies in the modeling.

A new edition of the HITRAN database was released on CD-ROM in 1996 (Rothman et al. 1998). HITRAN is now a component of a larger set of spectroscopic data and software called HAWKS (HITRAN Atmospheric Workstation). Details of the line-by-line portion of the compilation of spectroscopic parameters were described in the previous Atmospheric Radiation Measurement (ARM) Science Team Meeting. The goal of HITRAN and HAWKS is to provide a functional and flexible set of software and data in order to accurately model the simulation of transmission and radiance from the microwave through ultraviolet (UV) spectral regions. Besides an updated HITRAN high-resolution molecular database of about one million transitions, the compilation contains files of aerosol indices of refraction, UV line-by-line and cross-section parameters, supplemental files of gases that have undergone less validation or whose parameters require new definitions, such as ionic species, and extensive IR cross-sections now at different pressures and temperatures. In addition, the compilation contains a moderate-resolution band-model code, MODTRAN3. There is also vastly improved software handling of the data in both WINDOWS and UNIX platforms, such as more sophisticated selection filters, plotting capabilities, pointers to significant references, and documentation.

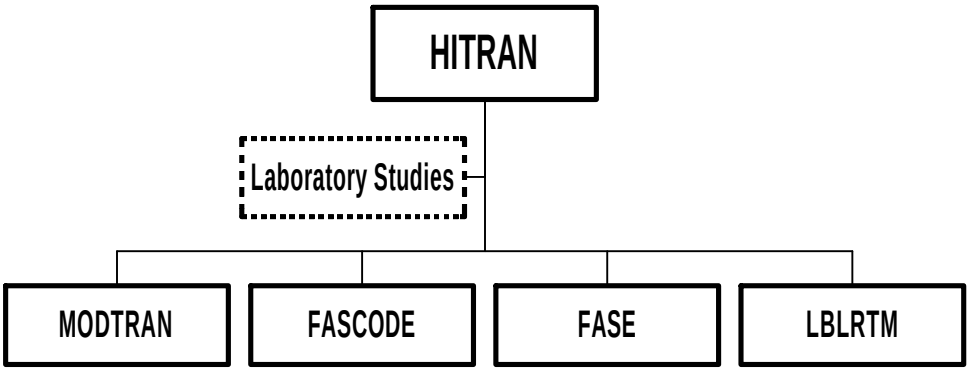


**Figure 1**. Interaction of HITRAN with codes and laboratory studies used in the ARM Program.

# IR Cross-Sections

When it became evident that data on individual spectral lines belonging to certain heavy molecular species such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), $SF_6$, and oxides of nitrogen (for example, $N_2O_5$) could not be reasonably characterized and tabulated in the traditional HITRAN format, the approach to report spectral absorption cross-sections measured at atmospheric conditions was adopted (Massie and Goldman 1992). The previous two editions of the HITRAN compilation (Rothman et al. 1987; Rothman et al. 1992) introduced temperature-dependent cross-sections but neglected the effect of pressure broadening. The increasing use of the cross-sections in atmospheric modeling, especially for remote sensing, has given rise to numerous laboratory programs for acquiring these data sets (Varanasi 1992a; Varanasi 1992b; Varanasi et al. 1992).

The absorption cross-section, $k_\nu$ ($cm^2$ $molecule^{-1}$), is defined as

$$k_\nu = (-\ln \tau_\nu)/\eta L$$

in terms of the spectral transmittance $\tau_\nu$ at the wavenumber $\nu$, temperature T, and pressure P, of column density $\eta$ (in molecule/$cm^3$) along an optical path of length L (cm). It is presented at several (T,P) combinations representing atmospheric layers given in commonly tabulated atmospheric models as well as conditions encountered in the polar regions.

Table 1 shows the datasets that have been added since the last edition of HITRAN. The cross-sections of CFC-11, CFC-12, HCFC-22, and $SF_6$ were provided by Varanasi et al. (1994), Varanasi and Nemtchinov (1994), and Li and Varanasi (1994). These cross-sections, as well as other cross-section data in HITRAN, were measured using high-resolution Fourier-transform spectrometers. For the four species listed above, a spectral resolution of 0.03 $cm^{-1}$ was adequate for most of the broadening pressures used in the experiments, while at 40 torr and lower, 0.01 $cm^{-1}$ was used. The data were obtained at temperatures between 200 K and 296 K and are free from instrumental distortion, because the spectra were recorded at a spectral resolution that was sufficiently high at each broadening pressure used. The bands of CFC-12 were measured in the 810 $cm^{-1}$ to 965 $cm^{-1}$ and 1040 $cm^{-1}$ to 1200 $cm^{-1}$ regions at temperatures ranging from 216 K to 296 K and pressures from 170 torr to 760 torr. The bands of CFC-11 in the 810 $cm^{-1}$ to 880 $cm^{-1}$ and 1050 $cm^{-1}$ to 1120 $cm^{-1}$ regions were measured at temperatures in the range from 201 K to 296 K and pressures between 40 torr and 760 torr. Measurements of HCFC-22 and $SF_6$ were made for bands in the 760 $cm^{-1}$ to 860 $cm^{-1}$ and 925 $cm^{-1}$ to 955 $cm^{-1}$ regions, respectively, at temperatures in the range from 216 K to 296 K and pressures from 40 torr to 760 torr.

The cross-sections for the $ClONO_2$ in the 1265 $cm^{-1}$ to 1325 $cm^{-1}$ region at 201 K, 211 K, and 222 K were provided by Orphal et al. (1994). They are made available along with those at 216 K and 296 K retained from the earlier editions of the database. The cross-sections of $CCl_4$, listed at room

**Table 1**. IR cross-section data added to latest editions of HITRAN.

| Molecule | Wavenumber Range ($cm^{-1}$) | Temperature Range (K) | Pressure Range (torr) | Number of P,T Panels |
|---|---|---|---|---|
| $CCl_4$ | 770-810 | 170-310 | — | 12[a] |
| CFC-11 | 810-880 | 201-296 | 40-760 | 33 |
| ($CCl_3F$) | 1050-1120 | 201-296 | 40-760 | 33 |
| CFC-12 | 810-965 | 216-296 | 170-760 | 15 |
| ($CCl_2F_2$) | 1040-1200 | 216-296 | 170-760 | 15 |
| HCFC-22 ($CHClF_2$) | 760-860 | 216-294 | 40-760 | 7 |
| $SF_6$ | 925-955 | 216-295 | 25-760 | 7 |
| $ClONO_2$ | 1265-1325 | 201-222 | — | 3[a] |
| HFC-32 | 995-1236 | 203-297 | 37-750 | 17 |
| ($CH_2F_2$) | 1385-1475 | 203-297 | 37-750 | 17 |
| HFC-134 ($CHF_2CHF_2$) | 600-1700 | 203-297 | 37-750 | 9 |
| HFC-143a | 580-630 | 203-297 | 37-750 | 9 |
| ($CF_3CH_3$) | 750-1050 | 203-297 | 37-750 | 9 |
| | 1100-1500 | 203-297 | 37-750 | 9 |

(a) Only temperature sets.

temperature in the previous editions of the database, have been augmented in this edition with data at 170 K, 223 K, 248 K, 273 K, 298 K, and 310 K reported by Orlando et al. (1992).

The data are presented as separate files for each individual molecule. Each portion of the file corresponding to a particular temperature-pressure pair begins with a header (see Table 2) that contains information on the wavenumber ($cm^{-1}$) range, number of cross-section data in this set, temperature (K), and pressure (torr). The maximum value of the absorption cross-section ($cm^2$/molecule) and additional information containing the reference to that observation are also presented in each header. The wavenumber spacing $\Delta\nu$ of the cross-section listings is uniform for each of the pressure-temperature sets, and is determined by taking the difference between the maximum and minimum wavenumber and dividing by one less the number of points N (cross-section data in this set), i.e., $\Delta\nu = (\nu_{max} - \nu_{min})/(N - 1)$.

**Table 2**. File structure and format (in FORTRAN) for cross-section files.

| **Molecule** **A10** | **$\nu_{init}$ (1) ($cm^{-1}$) F10.4** | **$\nu_{final}$ (1) ($cm^{-1}$) F10.4** | **Number of points I10** | ***T* (1) (°K) F10.4** | ***P* (1) (torr) F10.4** | **$\sigma_{max}$ E10.3** | **Reference + Additional Info. 3A10** |
|---|---|---|---|---|---|---|---|
| Cross-sections (10 per line) [ $cm^2$/molecule @ *T*(1),*P*(1) ] (10E10.3) | | | | | | | |
| **Molecule** **A10** | **$\nu_{init}$ (1) ($cm^{-1}$) F10.4** | **$\nu_{final}$ (1) ($cm^{-1}$) F10.4** | **Number of points I10** | ***T* (2) (°K) F10.4** | ***P* (2) (torr) F10.4** | **$\sigma_{max}$ E10.3** | **Reference + Additional Info. 3A10** |
| Cross-sections (10 per line) [ $cm^2$/molecule @ *T*(2),*P*(2) ] (10E10.3) | | | | | | | |
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| **Molecule** **A10** | **$\nu_{init}$ (2) ($cm^{-1}$) F10.4** | **$\nu_{final}$ (2) ($cm^{-1}$) F10.4** | **Number of points I10** | ***T* (1) (°K) F10.4** | ***P* (1) (torr) F10.4** | **$\sigma_{max}$ E10.3** | **Reference + Additional Info. 3A10** |
| Cross-sections (10 per line) [ $cm^2$/molecule @ *T*(1),*P*(1) ] (10E10.3) | | | | | | | |
| **Molecule** **A10** | **$\nu_{init}$ (2) ($cm^{-1}$) F10.4** | **$\nu_{final}$ (2) ($cm^{-1}$) F10.4** | **Number of points I10** | ***T* (2) (°K) F10.4** | ***P* (2) (torr) F10.4** | **$\sigma_{max}$ E10.3** | **Reference + Additional Info. 3A10** |
| Cross-sections (10 per line) [ $cm^2$/molecule @ *T*(2),*P*(2) ] (10E10.3) | | | | | | | |

Note: Data sets surviving from earlier editions are only given for different temperatures, not pressure-temperature pairs.

The increased use of hydrofluorocarbons (HFCs), which are expected to replace CFCs and HCFCs in many applications to reduce the deleterious effects of released chlorine on the atmospheric ozone layer, will add another absorber in the IR "window" region, 8 μm to 12 μm. Smith et al. (1998) have recently determined the cross-sections of HFC-134 ($CHF_2CHF_2$) and HFC-143a ($CF_3CH_3$), and these data will be available on a future edition of HITRAN.

# Conclusions

The HITRAN/HAWKS compilation has been steadily adding IR cross-sections for "heavy" molecular atmospheric species, where line-by-line parameters become highly impractical. The increased use of HFCs, which are expected to replace CFCs and HCFCs in many applications to reduce the deleterious effects of released chlorine on the atmospheric ozone layer, will add another absorber in the IR "window" region, 8 μm to 12 μm.

An example of new modeling capabilities is the methodology of line coupling, which has large implications in remote-sensing retrievals. A recent scheme by Rodrigues et al. (1998) has been developed that includes line-mixing parameters (as auxiliary files to HITRAN) as well as the software to properly use these parameters in radiative transfer codes.

Finally, all HAWKS software (editing, filtering, plotting, etc.) has been re-written in the JAVA language, so that one now has cross-platform conformity. This allows MAC users to have the full features of HAWKS that were only available previously in the WINDOWS and UNIX environments.

Updates are released for the HAWKS compilation on the HITRAN web site (*http://www.HITRAN.com*) prior to distribution of the final edition on CD-ROM. Other relevant information connected with the HITRAN spectroscopic database is also contained within this web-site.

# References

Li, Z., and P. Varanasi, 1994: Measurement of the absorption cross-sections of CFC-11 at conditions representing various model atmospheres. *JQSRT*, **52**, 137-144.

Massie, S. T., and A. Goldman, 1992: Absorption parameters of very dense molecular spectra for the HITRAN compilation. *JQSRT*, **48**, 713-719.

Orlando, J. J., G. S. Tyndall, A. Huang, and J. G. Calvert, 1992: Temperature dependence of the infrared absorption cross sections of the carbon tetrachloride. *Geophys. Res. Lett.*, **19**, 1005-1008.

Orphal, J., M. Morillon-Chapey, and G. Guelachvili, 1994: High-resolution absorption cross sections of chlorine nitrate in the $\nu_2$ band region around 1292 $cm^{-1}$ at stratospheric temperatures. *J. Geophys. Res.*, **99**, 14,549-14,555.

Rodrigues, R., K. W. Jucks, N. Lacome, Gh. Blanquet, J. Walrand, W. A. Traub. B. Khalil, R. Le Doucen, A. Valentin, C. Camy-Peyret, L. Bonamy, and J.-M. Hartmann, 1998: Model, software, and database for computation of line-mixing effects in infrared Q-branches of atmospheric $CO_2$. I. Symmetric isotopomers. *JQSRT*, accepted for publication.

Rothman, L. S., R. R. Gamache, A. Goldman, L. R. Brown, R. A. Toth, H. M. Pickett, R. L. Poynter, J.-M. Flaud, C. Camy-Peyret, A. Barbe, N. Husson, C. P. Rinsland, and M. A. H. Smith, 1987: The HITRAN database: 1986 Edition. *Appl. Opt.*, **26**, 4058-4097.

Rothman, L. S., R. R. Gamache, R. H. Tipping, C. P. Rinsland, M. A. H. Smith, D. Chris Benner, V. Malathy Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S. T. Massie, L. R. Brown, and R. A. Toth, 1992: The HITRAN molecular database: editions of 1991 and 1992. *JQSRT*, **48**, 469-507.

Rothman, L. S., C. P. Rinsland, A. Goldman, S. T. Massie, D. P. Edwards, J.-M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.-Y. Mandin, J. Schroeder, A. McCann, R. R. Gamache, R. B. Wattson, K. Yoshino, K. V. Chance, K. W. Jucks, L. R. Brown, V. Nemtchinov, and P. Varanasi, 1998: The HITRAN molecular spectroscopic database and HAWKS (HITRAN Atmospheric Workstation): 1996 Edition. *JQSRT*, **60,** in press.

Smith, K., D. Newnham, M. Page, J. Ballard, and G. Duxbury, 1998: Infrared absorption cross-sections and integrated absorption intensities of HFC-134 and HCF143a vapour. *JQSRT*, **59**, 437-451.

Varanasi, P., 1992a: Absorption coefficients of CFC-11 and CFC-12 needed for atmospheric remote sensing and global warming studies. *JQSRT*, **48**, 205-219.

Varanasi, P., 1992b: Absorption spectra of HCFC-22 around 829 $cm^{-1}$ at atmospheric conditions. *JQSRT*, **47**, 251-255.

Varanasi, P., A. Gopalan, and J. F. Brannon Jr., 1992: Infrared absorption coefficient data on $SF_6$ applicable to atmospheric remote sensing. *JQSRT*, **48**, 141-145.

Varanasi, P., and V. Nemtchinov, 1994: Thermal infrared absorption coefficients of CFC-12 at atmospheric conditions. *JQSRT*, **51**, 679-687.

Varanasi, P., Z. Li, V. Nemtchinov, and A. Cherukuri, 1994: Spectral absorption-coefficient data on HCFC-22 and $SF_6$ for remote-sensing applications. *JQSRT*, **52**, 323-332.