Instrumental line shape function for molecular line parameters retrieval, from high resolution Fourier transform spectra, for terrestrial or planetary atmospheric remote sensing

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I
MOTIVATION

The physico-chemistry of planetary atmospheres, and particularly the Earth's one, have been among the main subjects of studies over last years. For this purpose, remote sensing measurements by means of spectroscopic techniques has been established as an indispensable tool.

In spite of the improved Fourier Transform Spectrometers (FTS), and the advances in computational facilities, one requires the accurate knowledge of involved line parameters: positions, transition intensities, pressure-broadened half-widths, pressure-induced frequency shifts and their temperature dependence. In particular, the collisional broadening parameters have a crucial influence on the accuracy of spectra calculations and on reduction of remote sensing data.

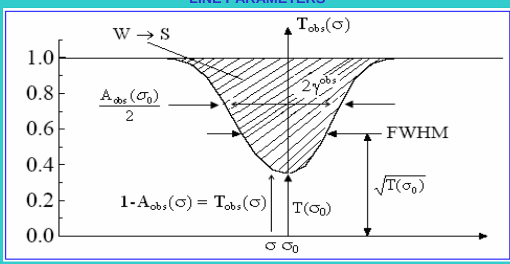
In laboratory spectroscopy, measurements of positions, intensities and other parameters of lines are in general long, very difficult, fastidious and even impossible for weak, blended, large, …, or superposed lines. That is why it is imperative to have theoretical models which permit calculating parameters. But models are reliable only if they are built up using correct data concerning line parameters. The correct data are obtained using adequate line profile (Lorentz, Voigt, Rautian, Galatry, Dicke, …) according to experimental conditions (temperature, pressures of absorbing gas and of buffer ones), and taking into account instrumental parameters for modeling a "realistic" Instrumental Line Shape (ILS) function.

Positions of lines produced by experiments are directly used to be fitted to quantum mechanical Hamiltonians. At the opposite, intensities, pressure broadening and pressure shifting are not directly used as produced by experiments, they can not be used as raw data. Hence, this crucial work located between experimentation and theoretical modeling of spectra is a vital intermediate step in the treatment of data. It requires the use of adequate, efficient, reliable computation codes adaptable to each particular case.

The computing method is adjusting a calculated spectrum to match the observed one, taking into account a comprehensive ILS function when necessary, by performing Non-Linear Least-Squares (NLS) procedures as:

• FitMas, Fit Molecular Absorption Spectra (F. Schreier).
• DUD, Doesn't Use Derivatives, an algorithm for non linear least squares fitting (V. Dana, J-Y Mandin, R.L. Hawkins,…, A. Hamdouni, M. Badaoui, M.-Y Allout, D. Jacquemart).

II
THEORETICAL TRANSMISSION AND LINE PROFILE CONSIDERED IN THIS WORK
LINE PARAMETERS



• Our purpose is to retrieve molecular line position, line strength, pressure broadening and pressure shifting : $\sigma_0, S_0, \gamma_L, \delta\sigma$

• The global response of the instrument or the so-called the local baseline $T_b(\sigma)$, around a position σ, is considered by adjusting the coefficients of an appropriate polynomial in wavenumber.

• The calculated transmission is the convolution product of the monochromatic transmission with the Instrumental Line Shape: $\frac{T^{cal}(\sigma)}{T_b(\sigma)} \approx T(\sigma) \otimes ILS(\sigma)$

• The monochromatic transmission is defined according to Beer-Lambert's law: $T(\sigma) = \frac{I}{I_0} = e^{-K(\sigma,P,T)\times \ell}$

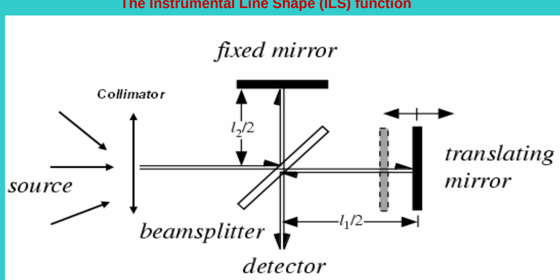
• $K(\sigma, P,T) = S_0 \times P_{gas} \times \Phi_V(\sigma, P)$ is the absorption coefficient. $\Phi_V(\sigma, P)$ is the normalized Voigt Line Profile.

$$\Phi_V(\sigma,P) = \frac{1}{\gamma_D}\sqrt{\frac{\ln(2)}{\pi}} \times \left(\frac{y}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-t^2)}{y^2+(x-t)^2}dt\right), \quad x = \sqrt{\ln(2)}\,\frac{\sigma-\sigma_o}{\gamma_D}, \quad y = \sqrt{\ln(2)}\,\frac{\gamma_D}{\gamma_L},$$
$$\gamma_D = \sqrt{\frac{2\ln(2)KT}{Mc^2}}\,\sigma_o \approx 3.58\times 10^{-7}\sqrt{\frac{T}{M}}\,\sigma_o$$

• If many lines (i) of diverse molecules (j) in different mediums (k) are considered:

$$T(\sigma) = e^{-[\sum_{k=1}^{N}\ell_k \times \sum_{j=1}^{n_k} P_{kj} \times \sum_i K^P_{\sigma(kji)}(T_K) \times \Phi_V(\sigma-\sigma_{0(kji)}, \gamma_{L(kji)})]}$$

III
The Instrumental Line Shape (ILS) function



• The Principle of Fourier Transform Spectrometer (FTS) is based on Michelson Interferometer.

• MICHELSON (1891): The spectrum is Fourier transform of the interferogram, $T(\sigma) = TF[I_o(\Delta)] = \int_0^{+\infty} I_o(\Delta)\times \mathrm{Cos}(2\pi\sigma\Delta)\,d\Delta$

• The path difference Δ of FT interferometer is limited between position zero and position maximum, $0 \le \Delta \le \Delta_{max}$, the first approximation of an ILS is then the sincBox function given by:

$$ILS(\sigma-\sigma_0) = FT[\Pi_{\Delta_{max}} \times I_{\sigma_0}(\Delta)] = FT[\Pi_{\Delta_{max}} \times \cos(2\pi\sigma_0\Delta)] = 2\Delta_{Max} \times \frac{\sin 2\pi(\sigma-\sigma_0)\Delta_{Max}}{2\pi(\sigma-\sigma_0)\Delta_{Max}} = 2\Delta_{Max} \times \mathrm{sinc}[2\pi(\sigma-\sigma_0)\Delta_{Max}]$$

1. The finite input iris gives rise to an optical apodization of the inteferogram $I_{\sigma_0}(\Delta)$ by the central arch of the following cardinal sine function [1,2]: $P(\Delta) = \mathrm{sinc}\left(\frac{\sigma_0\Omega\Delta}{2}\right) = \mathrm{sinc}\left(\frac{\sigma_0\Omega\Delta_{max}}{2}x\right), \quad \Omega = \pi\left(\frac{R}{F}\right)^2, \quad x = \frac{\Delta}{\Delta_{max}}$

where R is the iris radius and F is the focal length of the collimator. By developing P(x) in Taylor's series around x = 0, one obtains an $ILS(\sigma-\sigma_0) = f(\sigma-\sigma_0)$ that is symmetrical around the considered line σ_0.

2. The moving mirror position is inevitably affected by an error ε, the interferogram of a monochromatic line σ_0 is rather $I'(\Delta) = I(\Delta+\varepsilon)$ than $I(\Delta)$ only. The ILS is $FT[I'(\Delta)] = q(\sigma-\sigma_0) = f(\sigma-\sigma_0)\,\mathrm{Cos}\Phi + h(\sigma-\sigma_0)\,\mathrm{Sin}\Phi$, the phase error parameter is $\Phi = 2\pi\sigma_0\varepsilon$. $f(\sigma-\sigma_0)$ and $h(\sigma-\sigma_0)$ are the symmetrical and the anti-symmetrical parts of the ILS function [2-5].

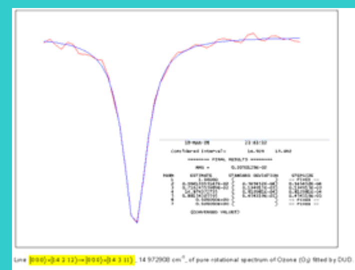
$$f(\sigma-\sigma_0) = \Delta_{max}\times D(u), \quad u = \pi(\sigma-\sigma_0)\times\Delta_{max}$$
$$D(u) = \frac{\mathrm{Sin}(2u)}{u}\left[\alpha+\beta\left(1-\frac{1}{2u^2}\right)+\gamma\left(1-\frac{3}{u^2}+\frac{3}{u^4}\right)+\delta\left(1-\frac{15}{2u^2}+\frac{45}{2u^4}-\frac{45}{4u^6}\right)\right] + \frac{\mathrm{Cos}(2u)}{u}\left[\frac{\beta}{u}+\gamma\left(\frac{2}{u}-\frac{3}{u^3}\right)+\delta\left(\frac{3}{u}-\frac{15}{u^3}+\frac{45}{2u^5}\right)\right],$$
$$\theta = \sigma_0\Omega\frac{\Delta max}{2}, \quad \alpha = 1, \quad \beta = -\frac{\theta^2}{3!}, \quad \gamma = \frac{\theta^4}{5!}, \quad \delta = -\frac{\theta^6}{7!}$$

$$h(\sigma-\sigma_0) = \Delta_{max}\times E(u)$$
$$E(u) = \frac{\mathrm{Sin}(2u)}{u}\left[\frac{\beta}{u}+\gamma\left(\frac{2}{u}-\frac{3}{u^3}\right)+\delta\left(\frac{3}{u}-\frac{15}{u^3}+\frac{45}{2u^5}\right)\right] - \frac{\mathrm{Cos}(2u)}{u}\left[\alpha+\beta\left(1-\frac{1}{2u^2}\right)+\gamma\left(1-\frac{3}{u^2}+\frac{3}{u^4}\right)+\delta\left(1-\frac{15}{2u^2}+\frac{45}{2u^4}-\frac{45}{4u^6}\right)\right] + \frac{1}{u}\left[\alpha-\frac{\beta}{2u^2}+\frac{3\gamma}{2u^4}-\frac{45\delta}{4u^6}\right],$$
$$\theta = \sigma_0\Omega\frac{\Delta max}{2}, \quad \alpha = 1, \quad \beta = -\frac{\theta^2}{3!}, \quad \gamma = \frac{\theta^4}{5!}, \quad \delta = -\frac{\theta^6}{7!}$$

3. If the distortions of the spectrum are due to variations of the experimental conditions, during the recording of the interferogram, inside the absorption cell (partial pressures and temperature)[6], or outside the cell[7-8], $f(\sigma-\sigma_0)$ and $h(\sigma-\sigma_0)$ function will be more expanded and complicated.
4. If the non-multiplying channelling arises, the ILS will be also somehow $q'(\sigma-\sigma_0) = f'(\sigma-\sigma_0)\cos\Phi' + h'(\sigma-\sigma_0)\sin\Phi'$. Φ' is then the channel parameter[4].

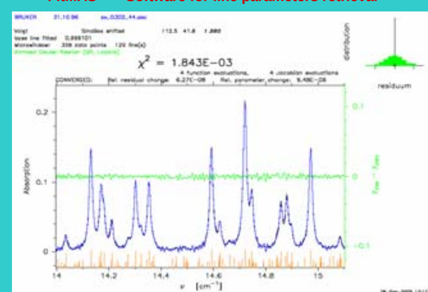
IV
PROGRAM DUD[9-10]
A MODIFIED RALLSTON- JENNRICH DUD (DUD = Does not Use Derivatives) ALGORITHM FOR NON LINEAR LEAST SQUARES FITTING.

• To measure accurate line parameters, the "true" instrument line shape function of the FTIR spectrometer must be known, especially for no commercial, home built, instruments.
• The ILS is usually calculated from "known" spectrometer parameters, such as the maximum optical path difference, the iris input diameter, and the focal length of the collimator to take into account the optical apodization and the phase error. The internal non multiplying channel, if any, is considered. The obtained theoretical ILS is convolved with the monochromatic transmission to provide a theoretical transmission that is fitted to match the observed transmission to retrieve line parameters.
• The Voigt function is calculated using the Gautschi's algorithm [11-12].
• Nonlinear least squares procedures (NLS) require an initial guess of model's parameters to be fitted in the iterative process[13]: for DUD, initial line parameters are provided by computational code Derpth of Dr. Delouis[14]. One can also successfully use initial guess of parameters readen from peaklists supplied by experimentalists.



• The second parameter of the fit is $S_0 P\ell$ given in cm^{-1} at the experimental temperature (here 296.26 K).

V
FitMAS[15-16] Software for line parameters retrieval



The same line, |14, 2, 12> → |14, 3, 11> fitted, among others, by FitMAS

• The FitMAS — Fit Molecular Absorption Spectra code - performs a nonlinear least squares (NLS) fit to determine molecular spectral line parameters from observed Fourier transform spectra.
• In FitMAS, the (NLS) procedure is around Gauss-Newton or Levenberg-Marquardt methods algorithm based on the Minpack routine[16].
• In addition to Lorentz and Voigt line shapes, several alternatives can be used appropriate to model collisional narrowing effects, e.g., correlated and uncorrelated Rautian profiles[17].
• For the ILS either a simple sinc function (accounting for the finite optical path difference Δ_{max} of the FTS), a convolution of sinc and boxcar $\Pi_{\Delta max}$ (additionally accounting for the finite input iris whose radius R is fitted if necessary) or a phase distorted sinc are possible options.
• The baseline effects $T_b(\sigma)$ can be considered by adjusting the coefficients of an appropriate polynomial in wave number.
• Jacobians, i.e., derivatives of the model function with respect to the parameters to be fitted, are computed fully analytically, hence avoiding the numerical delicacies of finite differences and resulting in a considerable computational efficiency gain[18-20]. Furthermore it should be noted that the convolution integral of monochromatic transmission and instrumental line shape is evaluated exactly.
• Nonlinear least squares fits require an initial guess of parameters to be fitted in the iterative process: For FitMAS[20], line parameters can be read from HITRAN[22] and JPL–type[23] databases, or from simple peaklists.

VI
Experimental conditions of one spectrum SX_O3O2_44[24]

Spectrum	MOPD (cm)	Primary step 10^{-3} cm^{-1}	P 10^{-3} bar	ℓ (cm) short cell	T(K)	Iris Radius (mm)	Focal length (mm)
SX_O3O2_44	112.5	3.0904289	$P(O_3)$=35.38(35) + $P(O_2)$=51.44(46) + $P(N_2)$=0.0	24.9 ± 0.0	296.26 ± 0.0	given 6.4 ± 0.0	418.0 ± 0.2

VII
A sample of line parameters retrieved, by two methods, from the spectrum above

Rotational transition[25-26]	Line σ_0 (cm^{-1})	DUD $S_0 \times 10^{-3}$	FitMAS $S_0 \times 10^{-3}$	HITRAN (1996) $S_0 \times 10^{-3}$
14 2 12 → 14 3 11	14.972908	4.18	4.16	4.19
12 2 10 → 12 3 9	15.25770	4.10	4.04	4.04
17 2 16 → 17 3 15	16.25620	4.89	4.69	4.73
25 1 25 → 25 2 24	17.82140	2.49	2.51	2.57
28 0 28 → 28 1 27	17.87650	1.83	1.87	1.97

Absolute strengths are given in cm^{-2} atm^{-1} at 296.26K.
Unit conversion formulas are taken from reference [27].

References

1. James W. Brault, lectures on Fourier Transform Spectrometry, National Solar Observatory Tucson, Arizona 85728, USA (1985)
2. V. Dana and J, -Y. Mandin, New improvement in the determination of line parameters from FTS DATA, J. Quant. Spectrosc. Radiat. Transfer Vol. 48, No. 5/6, pp. 725-731, 1992
3. M. Badaoui, lecture on parameters retrieval from lines in high resolved spectra, obtained by Fourier transform spectrometer. Examples: C_3H_8 in high resolution spectrum of Titan, and $^{14}HN^{16}O_3$ in Earth's atmospheric spectra. International Astronomical Union (IAU), 27th ISYA, Al Akhawayn University, Ifrane, Morocco, July 02-23, 2004.
4. M. Badaoui, Doctoral thesis, Paris (1993).
5. M. Badaoui, M. Alaoui Elbelghiti, Phys. Chem. News 21 (2005) 94-100.
6. Dana, V., Mandin, J.-Y., Allout, M.-Y. and Régalia, L., JQSRT, 1996, 56, 119.
7. M-Y. Allout, J-Y. Mandin, V. Dana, N. Picqué and G. Guelachvili, FTS Generalised apparatus function, J.Quant.Spectrosc.Radiat.Transfer Vol. 60, No 6, pp. 979-987, 1998
8. M-Y. Allout, Doctoral thesis, Paris (1998).
9. Mary L. Ralston and Robert I. Jemrich, Technometrics, Vol. 20, No 1, February 1978.
10. B. H. Armstrong, J. Q. S. R. T., 7, 61 (1967).
11. W. Gautschi, Algorithm 363, Complex error function, Communication of the ACM 1969; 12:635.
12. Fc and W. Gautshi, SIAM J. Numer. Anal., 7, 187 (1970).
13. K. S. Kölbig, Com. ACM, 15, 465 (1972).
14. H. Delouis, Doctorat de 3ème Cycle, Université de Paris VI (1968). H. Delouis, Doctorat d'Etat, Université de Paris-Sud (1973)
15. F. Schreier, B. Schimpf, and M. Birk, FITMAS - Least squares fitting of molecular line parameters from high resolution Fourier transform spectra, Poster M13 in XIII. Colloquium on High Resolution Molecular Spectroscopy, Riccione, Sept. 1993.
16. G. Wagner, M. Birk, F. Shreier, and J. –M. Flaud, Spectroscopic database for ozone in the fundamental spectral regions, J. Geophys. Res. 107 (D22):4626, doi: 10.1029/2001JD000818 (ACH – 10-1 -10-18)2002.
17. J.E. Dennis and R.B. Schnabel, Numerical Methods for Unconstrained Optimization and linear Equations. Prentice-Hall, 1983.
18. P.L. Varghese and R.K. Hanson, Collisional narrowing effects on spectral line shapes measured at high resolution. App. Opt., 23:2376-2385, 1984.
19. F. Schreier, the Voigt and Complex Error Function: A Comparison of Computational Methods. J. Quant. Spectros. Radiat. Transfer. 48, 743 (1992).
20. J.W.C. Johns, F. Schreier, B. Schimpf, and M. Birk, analysis of High-Resolution Fourier Transform Molecular Spectra.In The Future of Spectroscopy: From Astrophysics to Biology, Quebec, September 1994.
21. F. Schreier and B. Schimpf, FITMAS - Least squares fitting of molecular line parameters from high resolution Fourier transform spectra - Description and User's Guide. DLR - internal report, 1995.
22. L.S. Rothman et al. (31 authors), J. Quant. Spectrosc. & radiat. Transfer. 82: 5-44 (2003).
23. H.M. Pickett, R.L. Poynter, E.A. Cohen, M.L. Delitsky, J.C. Pearson, and H.S.P. Müller. Submillimeter, millimeter, and microwave spectral line catalog. J. Quant. Spectrosc. & Radiat. Transfer. 60:883-890, 1998.
24. Pure rotational O_3 (mixed with O_2, N_2 and the air) spectra recorded by G. Wagner and M. Birk from DLR, German Aerospace Center, Remote Sensing Institute, Oberpfaffenhofen, D-82234 Wessling, Germany.
25. Dr. Semen N Mikhailenko, Institute of Atmospheric Optics (LTS),, Tomsk, Russia. Private communication 18 April 2006.
26. G.N. Mikhailenko, Yu.L. Babikov and V.F. Golovko, Information-calculating system spectroscopy of Atmospheric Gases. The structure and main functions, vol.18, No. 9/September 2005/Atmos. Ocanic Opt. 685.
27. L.A. Pugh and K.N. Rao. Intensities from infrared spectra. In K.N. Rao, editor, Molecular Spectroscopy: Modern Research, volume II, pages 165-227. Academic Press, 1976.