July 2007

Phys. Chem. News 36 (2007) 01-09 PCN

RETRIEVAL OF LINE PARAMETERS FROM HIGH RESOLUTION FOURIER TRANSFORM LABORATORY SPECTRA IN SUPPORT OF ATMOSPHERIC SPECTROSCOPY

M. Badaoui[1]*, F. Schreier[2], G. Wagner[2], M. Birk[2]

[1] *IAV Hassan II, Physics Unit, B.P. 6240, Madinat Al-Irfane, 10101 Rabat-Morocco*

[2] *DLR-Remote Sensing Technology Institute, Oberpfaffenhofen, D-82234 Wessling, Germany*

** Corresponding author. E-mail: nouralhakim@yahoo.com*

Received: 31 March 2006; revised version accepted: 22 June 2006

Abstract

Fourier transform infrared (FTIR) spectroscopy has become a powerful tool for the detection and measurement of gas emissions (or absorption) in terrestrial and planetary atmospheric remote sensing. Besides the improving quality of current instruments (signal to noise ratio, spectral resolution, sensors' response…) and the advances in computational facilities, one needs precise knowledge of molecular spectroscopic line parameters to deduce accurate atmospheric state (e.g., temperature and molecular concentrations). Consequently, scientific studies of the major environment questions of global warming and Ozone depletion require global precise datasets of atmospheric constituents. These databases are supplied with molecular line parameters from laboratory spectroscopy. In fact, measurements of positions, intensities, pressure broadening and pressure shifting coefficients…or 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 these parameters. But models are reliable only if they are built up using correct data concerning line parameters obtained by using adequate line shape as Lorentz, Voigt, Rautian, Galatry, Dicke profiles…according to experimental conditions (e.g. temperature, pressure, buffer gases,…), and taking into account instrumental parameters for modeling the Instrumental Line Shape (ILS).

Positions of lines produced by experiments are directly used to determine quantum mechanical Hamiltonians'constants. At the opposite, intensities, pressure broadening and pressure shifting aren't directly used as produced by experiments. They can't be used as raw data.

This crucial work located between the experimentation and the theoretical modeling of spectra is a vital intermediate step in the treatment of the data. It needs the use of adequate, efficient, reliable computation codes adaptable to each particular case. Here we describe this intermediate work. As example, we retrieve line parameters of few lines of a pure rotational spectrum of Ozone molecule (O_3). For this purpose, we use two codes for line parameters retrieval developed independently:

1. FitMas, Fit Molecular Absorption Spectra developed by F. Schreier.
2. DUD algorithm, Doesn't Use Derivatives, for non linear least squares fitting used by M. Badaoui.

Keywords : Fourier Transform Spectrometer (FTS); Line Parameters (line position; Strength; Pressure-broadening and pressure shifting) ; Voigt profile; Instrumental Line Shape (ILS); finite aperture of the FTS or optical apodization; Error on the position of the movable mirror of the FTS or phase error; Pure rotational spectrum of ozone (O_3).

1. Principle of line parameters measurement method

In order to obtain precise line parameters, we fit a computed spectrum to the experimental one by performing a non-linear least squares method (NLS), and using an effective ILS and an adequate line profile.

1. In FitMas [1-2], the NLS problem is solved iteratively using a Gauss-Newton or Levenberg-Marquardt trust region algorithm based on the Minpack routine [3].

Lorentz, Voigt, and several alternatives line profiles can be used appropriately to model collisional narrowing effects, e.g., correlated and uncorrelated Rautian profiles [4].

For the ILS either a simple sinc function, a convolution of sin and box $\Pi_{\Delta max}$, accounting for the finite optical path difference Δmax of the FTS, additionally accounting for the finite input iris whose radius R is fitted if necessary, or a phase distorted sinc are possible options [5].

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 [5-7]. Furthermore it should be noted that the convolution integral of monochromatic transmission and instrumental line shape is evaluated exactly.

All nonlinear least squares fits require an initial guess of the parameters to be fitted in the iterative process: For FitMas, initial line parameters can be read from HITRAN [8], JPL–type [9] databases, or simple peaklists from experiments.

2. In the method based around DUD core, the fitting program adjusts a computed profile to the experimental one using a NLS procedure based on a derivative-free algorithm described in Ref. [10]. For the moment, the only line shape considered here is Voigt profile calculated using the Gautschi's algorithm [11- 17].

To measure accurate line parameters, the true ILS or the response function of the FTIR spectrometer must be known, especially for laboratory built instruments. So, at the beginning, the ILS is conceived for Connes [18] type Michelson interferometers. More precisely, the ILS 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 also considered. Afterwards, the obtained theoretical ILS is convolved with the modeled transmission to provide a calculated transmission that is fitted to the observed transmission to retrieve line parameters.

Initial guess of parameters to be fitted in the iterative process for DUD is provided by the pointing program code of H. Delouis [19-20] that determines rough values for the position, intensity, and collisionnal width of lines arising in the experimental spectrum.

Around a line σ, the global instrumental response (windows, filters and sensors) or what we call the baseline effect, is a multiplying factor that can be considered by adjusting the coefficients (a, b, c) of an appropriate local polynomial in wave number, $T_b(\sigma) = a\times\sigma^2 + b\times\sigma + c$, in both FitMas and DUD methods.

2. Beer-Lambert's law, Voigt profile and the theoretical transmission

The theoretical transmission (Fig.1.) of light through a layer ℓ of gas is given by the Beer-Lambert's law $T_{th}(\sigma) = \frac{I_t(\sigma)}{I_0(\sigma)} = \exp\left[-k(\sigma, P, T)\ \ell\right]$.

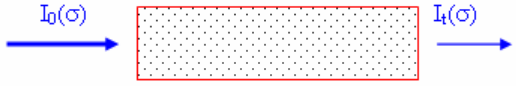

Figure 1.

Absorption cross section, k(σ, P, T), depends upon temperature and pressure of the absorbing gas. The intensity (or strength) of a line is the integrated coefficient of the absorption given by the expression $S = \int_0^{\infty} K(\sigma, P, T)\, d\sigma$. In the frame of this work, the temperature is constant during the experiment and the pressure P is lower than 1 atm., one can assume $S \approx S_0 P$. The coefficient of the absorption K(σ, P) is the Voigt profile which is the convolution between the Gauss' profile and the Lorentz's profile.

The expression of Voigt profile is

$$K_V(\sigma, P) = So\, P \frac{1}{\gamma_D}\sqrt{\frac{\ln(2)}{\pi}}\frac{y}{\pi}\int_{-\infty}^{\infty}\frac{e^{(-t^2)}}{y^2 + (x-t)^2}dt,$$

$$x = \sqrt{\ln(2)}\frac{\sigma - \sigma_0}{\gamma_D} \text{ and } y = \sqrt{\ln(2)}\frac{\gamma_L}{\gamma_D}.$$

In DUD method, the Doppler broadening is fixed to the following approximate value:

$$\gamma_D = \sqrt{\frac{\ln(2)\, k\, T}{Mc^2}}\sigma_0 \approx 3.58\times10^{-7}\sqrt{\frac{T}{M}}\sigma_0$$. M is the molar mass and T is the temperature in Kelvin degree. The algorithm of Gautschi is used to retrieve the absolute position σ_0, the collisional width γ_L, the relative intensity S, and the absolute intensity S_0 if the pressure P of the absorbing (or emitted) gas and the optical length ℓ in the cell are well known.

3. The instrumental effects for programs chain around DUD core

3.1 The theoretical ILS

The observed transmission $T_{obs}(\sigma)$ is the convolution between the theoretical transmission and the ILS(σ) of the Fourier Transform Spectrometer (FTS), or so called the response function of the instrument here noted $f_{app}(\sigma)$:

$$T_{obs}(\sigma) = T_{th}(\sigma) \otimes f_{app}(\sigma) = \int_{\Delta\sigma} T_{th}(\sigma') f_{app}(\sigma - \sigma')d\sigma' .$$

Δσ is the spectrum range considered around the line σ. Parameters of the line are retrieved by fitting the experimental line $T_{exp}(\sigma)$ to the observed one $T_{obs}(\sigma)$ defined by the above expression. In Fourier transform spectroscopy when no numerical apodization of the interferogram is performed, the theoretical apparatus function is $\sin c(x) = \frac{\sin(x)}{x}$ type function with a full width at half maximum of about $R_{th} = \frac{1}{2\Delta_{max}}$, Δ_{max} being the maximum path difference. R_{th} is the theoretical resolution of the instrument.

3.2 The optical apodization or the through-put effect

Because of the finite radius of the input iris, the source beam is not a pencil one. It is not a Dirac peak. Consequently, the optical apodization due to the through-put has to be taken into account. Its effect could be huge according to the spectrum range. Considering only the through-put effect, the ILS expression used in DUD method [21] is the following function $f(\sigma - \sigma_0)$:

$$f(\sigma-\sigma_0)=\Delta_{max}\times D(u),\ u=\pi(\sigma-\sigma_0)\times\Delta_{max}$$

$$D(u)=\frac{\sin(2u)}{u}\left[\alpha+\beta\left(1-\frac{1}{2u^2}\right)+\gamma\left(1-\frac{3}{u^2}+\frac{3}{2u^4}\right)+\delta\left(1-\frac{15}{2u^2}+\frac{45}{2u^4}-\frac{45}{4u^6}\right)\right]+\frac{\mathrm{Cos}(2u)}{u}\left[\frac{\beta}{u}+\gamma\left(\frac{2}{u}-\frac{3}{u^3}\right)+\delta\left(\frac{3}{u}-\frac{15}{u^3}+\frac{45}{2u^5}\right)\right]$$

with $\theta=\sigma_0\,\Omega\frac{\Delta_{max}}{2}$, $\alpha=1$, $\beta=-\frac{\theta^2}{3!}$, $\gamma=\frac{\theta^4}{5!}$ and $\delta=-\frac{\theta^6}{7!}$.

Note that if we neglect the optical apodization in the above expression, $\beta=\gamma=\delta=0$, we will find the unapodized symmetrical part of the ILS: $D(u)=\frac{\sin(2u)}{u}$.

The solid angle $\Omega=\pi\left(\frac{R}{F}\right)^2$ of the light beam is defined by the iris radius R and by the focal length F. The typical collimator focal length of the Brüker Fourier transform instrument is F = 41.80 cm. However, the parameter R is not precise. It is often fitted around a trusted value. The apparatus function is calculated for each line σ_0 and numerically normalized.

3.3 The phase error

Error on the position of the movable mirror of the interferometer inevitably occurs. This error is called a phase error and leads to a slightly asymmetrical apparatus function whose expression, if we do not take into account at the same time the through-put effect, is:

$$u=\pi\times(\sigma-\sigma_0)\times\Delta_{max}$$

$$q(\sigma-\sigma_0)=\cos\Phi\times f(\sigma-\sigma_0)+\sin\Phi\times h(\sigma-\sigma_0)$$

$$=\cos\Phi\times\left[\Delta_{max}\times\frac{\sin(2u)}{u}\right]+\sin\Phi\times\left[\Delta_{max}\times\frac{1-\cos(2u)}{u}\right].$$

The unapodized antisymetrical part of the apparatus function is:

$$h(\sigma-\sigma_0)=\Delta_{max}\times\left[\frac{1-\mathrm{Cos}(2u)}{u}\right].$$

If the path difference Δ is affected by an error ε, Δ $\rightarrow$ Δ + ε, the phase error is $\Phi=2\pi\sigma_0\varepsilon$ [22].

The parameter of the asymmetry Φ is adjustable in order to obtain the best fit.

The phase error induces errors on position determination and consequently on pressure broadening and pressure shifting coefficients. Errors increase with the line width 2γ and with the maximum path difference Δ_{max}. We remind that at the opposite of the phase error, the through-put has an effect on the intensities measurement. Consequently the ILS' expression taking into account the two effects, the optical apodization and the phase error, is approximately a realistic one and is given by the following formulae:

$q(\sigma-\sigma_0) = f(\sigma-\sigma_0)\times\cos\phi + h(\sigma-\sigma_0)\times\sin\phi$. The function $f(\sigma-\sigma_0)=\Delta_{max}\times D(u)$ is already discussed in (§ 3.2.).

$$h(\sigma-\sigma_0)=\Delta_{max}\times E(u)$$

$$E(u)=\frac{\sin(2u)}{u}\times\left[\frac{\beta}{u}+\gamma\left(\frac{2}{u}-\frac{3}{u^3}\right)+\delta\left(\frac{3}{u}-\frac{15}{u^3}+\frac{45}{2u^5}\right)\right]-$$

$$\frac{\cos(2u)}{u}\times\left[\alpha+\beta\left(1-\frac{1}{2u^2}\right)+\gamma\left(1-\frac{3}{u^2}+\frac{3}{2u^4}\right)+\delta\left(1-\frac{15}{2u^2}+\frac{45}{2u^4}-\frac{45}{4u^6}\right)\right]+\frac{1}{u}\times\left[\alpha-\frac{\beta}{2u^2}+\frac{3\gamma}{2u^4}-\frac{45\delta}{4u^6}\right]$$

where $\theta=\sigma_0\,\Omega\frac{\Delta_{max}}{2}$, $\alpha=1$, $\beta=-\frac{\theta^2}{3!}$, $\gamma=\frac{\theta^4}{5!}$, $\delta=-\frac{\theta^6}{7!}$.

3.4 Other instrumental effects

Finally, one should not forget the determination of the zero transmission level that could be wrong for different experimental reasons, especially electronic ones.

The error of the zero transmission is determined by saturated lines, not necessary of the absorbing gas.

4. The instrumental effects in FitMas [5]

4.1 The theoretical ILS

The theoretical instrumental line shape is the same for any Michelson type interferometer:

$$R(\sigma-\sigma_0)=\frac{\sin\left[2\times\pi\times\Delta_{max}\times(\sigma-\sigma_0)\right]}{\pi\times(\sigma-\sigma_0)}$$
$$=2\times\Delta_{max}\times\mathrm{sinc}\left[2\times\pi\times\Delta_{max}\times(\sigma-\sigma_0)\right].$$

4.2 The finite entrance in FitMas, equivalent to the through-put effect IN DUD

Now we consider a finite entrance (aperture) with radius R, we define the small angle $\alpha\approx\frac{R}{F}$ and $\mathrm{Si}(x)=\int_0^x\frac{\sin t}{t}dt$. After normalization and calibration, the general ILS in FitMas is given by:

$$R(\sigma,\sigma_0)=\frac{2(1-\frac{\alpha^2}{4})}{\pi\alpha^2\sigma_0}\times\left\{\begin{array}{l}\mathrm{Si}\left[2\pi\Delta_{max}\left[\sigma(1-\frac{\alpha^2}{4})-\sigma_0(1-\frac{\alpha^2}{2})\right]\right]\\-\mathrm{Si}\left[2\pi\Delta_{max}\left[\sigma(1-\frac{\alpha^2}{4})-\sigma_0\right]\right]\end{array}\right\}.$$

Note the $(1-\frac{\alpha^2}{4})$ factor which has been introduced to conserve the normalization of the ILS.

4.3 The phase error

Assuming a non-frequency dependant phase error ε, the ILS in FitMas is :

$$\Phi=2\pi\sigma_0\varepsilon$$
$$R(\sigma)=2\Delta_{max}\left(\begin{array}{l}\cos\Phi\times\left[\frac{\sin(2\pi\Delta_{max}\sigma)}{2\pi\Delta_{max}\sigma}\right]\\+\sin\Phi\times\left[\frac{\mathrm{Cos}(2\pi\Delta_{max}\sigma)-1}{2\pi\Delta_{max}\sigma}\right]\end{array}\right).$$

5. Flow diagram of 'DUD core's method

The sources code of programs are written in FORTRAN. A pointing program of H. Delouis [19-20] determines rough values for position, intensity, and collisional width of lines arising in the experimental spectrum. The selecting program selects the line to be studied and creates a file of initial parameters used in the fitting program. We precise for the selecting program a spectral range δσ over which the lines are fitted simultaneously around the desired line, and a larger range Δσ for which the influence of the lines is taken into account. Δσ includes of course δσ [Fig.2]. Otherwise, all parameters of lines belonging to δσ are free, and parameters of lines belonging to Δσ – δσ are fixed to their values determined in the precedent iteration. The fitting program adjusts a computed profile to the experimental one using the DUD [10] least-squares fitting procedure. Finally the computed profile is obtained by convolving the theoretical line shape, described here by Voigt profile, with the instrumental line shape (ILS) taking into account the optical apodization and the phase error. [Fig.3] shows the flow diagram.

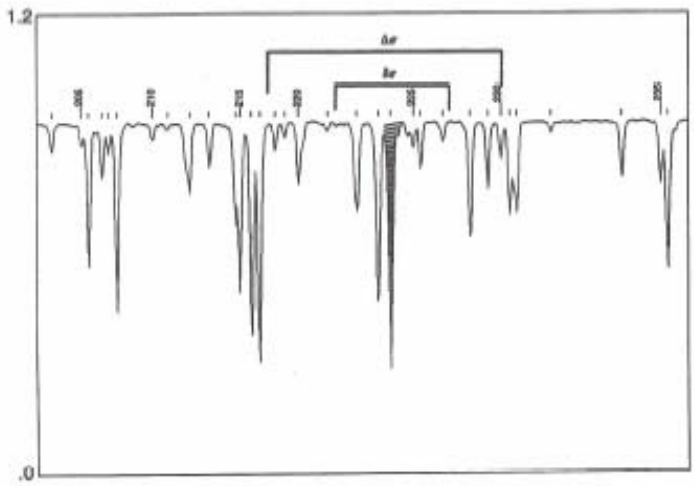

Figure 2: Principle of selecting program Scanned from Ref. [23]

6. Application to some MW lines intensities of O_3 around 14.5 cm^{-1}

Our goal in this work is updating and developing sources code of programs, around DUD core, of line parameters retrieval and applying them to any work as demonstrations. Otherwise, our present study is essentially undertaken to test chain of programs devoted to line parameters measurement (especially intensity) in the case of Voigt profile. Afterwards, we compare obtained intensities of some lines with those obtained by FitMas. We note in [Fig.4-5]

that the continuous background is almost a straight line, therefore the baseline can be considered as a constant, $T_b(\sigma) = C^{te}$.

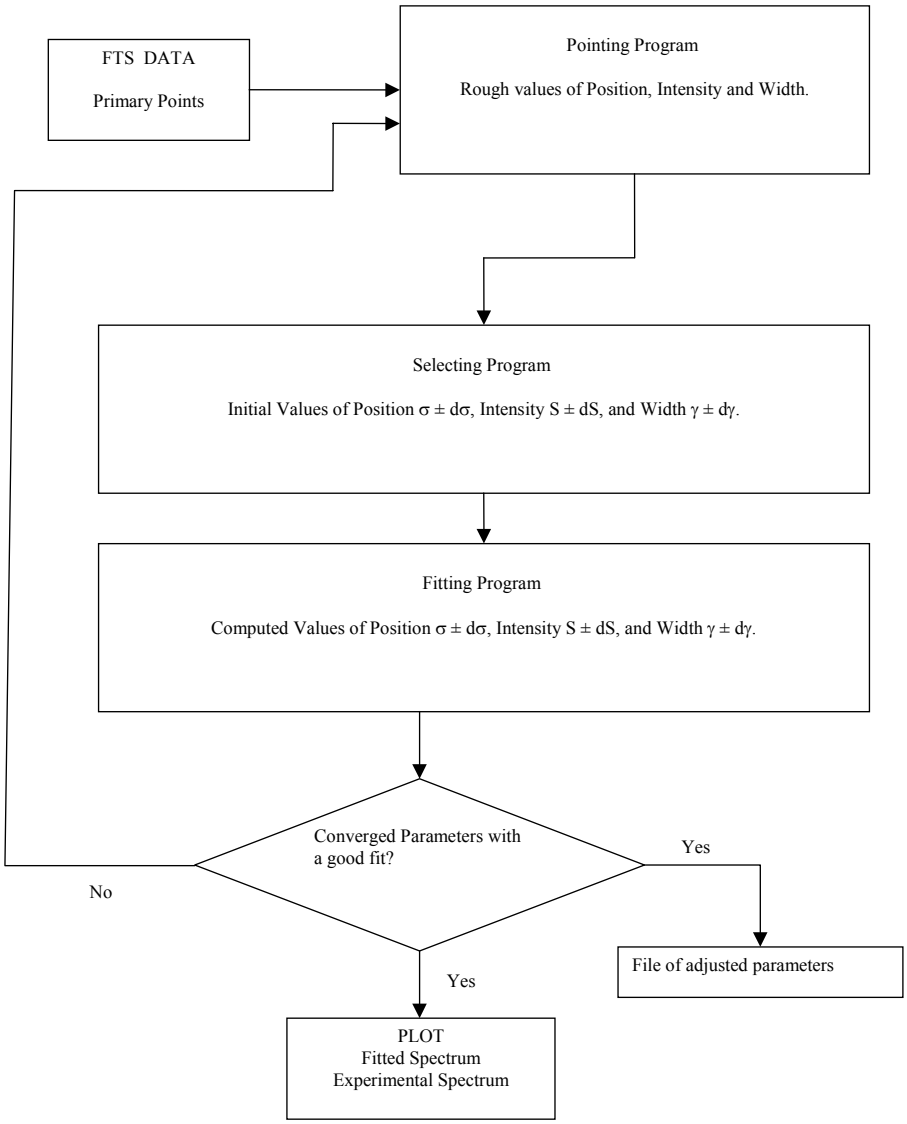

Figure 3: Flow diagram [23]. Line parameters measurement from FTS data.

The fit by DUD and by FitMas of the line shown in [Fig. 5] are successively displayed in [Fig. 6. and Tables. 1-2.] and [Fig.7]. The result of the fit is given in Tables 1-2 that shows well converged values of parameters.

In spite of the good quality of the signal to noise ratio (SNR ≥ 300), DUD is very sensitive to noise as shown in the wing of the line. Fig. 6.

We note the power of FitMas Software that fits many lines in a window with amplitude of residuals less than 1.0 % even in the case of noise [Fig.7].

DUD also can be managed to fit a set of lines. Both programs converges with RMS around 2×10^{-3}.

The experimental conditions are consigned in Table 3.

In Table 4 are given some lines' absolute intensities measurement for comparison.

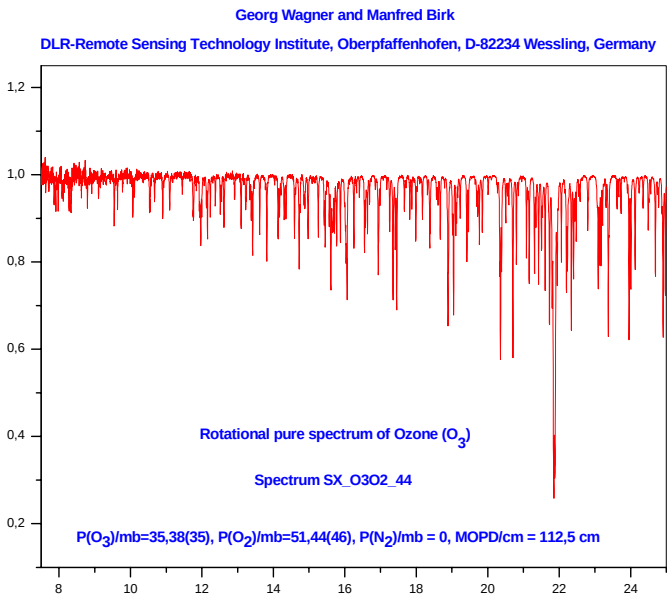

Figure 4 : Absorption spectrum A (σ). A survey of pure rotational spectrum of of O_3 around 16 cm^{-1}.

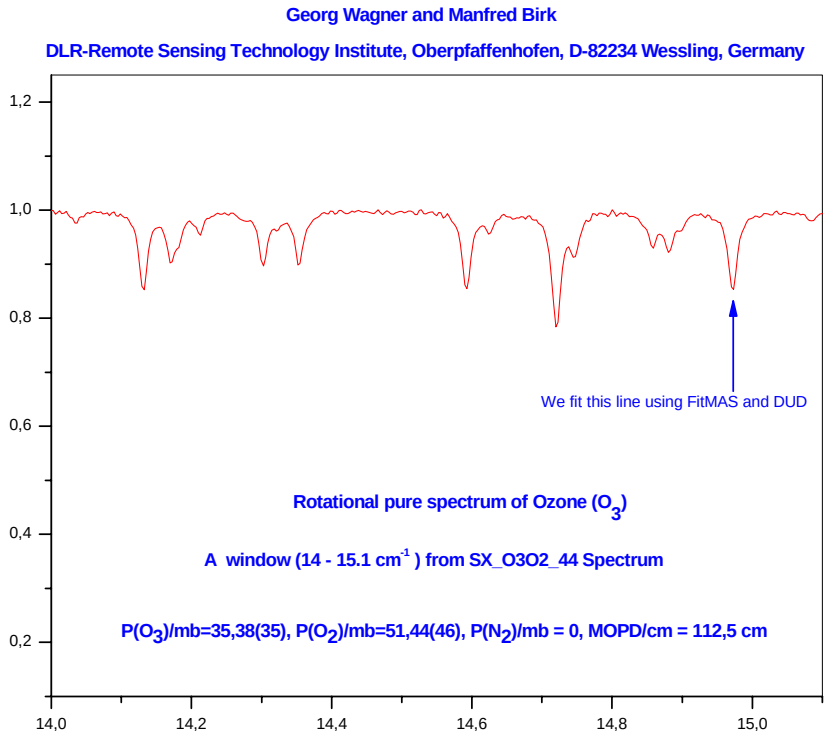

Figure 5: A selected absorbing line to be fitted by FitMas and DUD for comparison.
The pointed line is: $\left|v_1, v_2, v_3, J, K_a, K_c\right\rangle = \left|0,0,0,14,2,12\right\rangle \rightarrow \left|0,0,0,14,3,11\right\rangle \Rightarrow \sigma_0 = 14.973\,cm^{-1}$.

```
                    26-JUN-06          12:52:05
          Considered Interval: Δσ=δσ= 14.924 - 15.016
       ======== FINAL RESULTS (CONVERGED VALUES) ========

                  RMS =    0.1915196E-02
PARM          ESTIMATE          STANDARD DEVIATION    STEPSIZE
  1               1          :                     : -- FIXED --
  2       0.35913745093E-02 :    0.613162E-04     : 0.613162E-04
  3       0.70768479162E-02 :    0.141268E-03     : 0.141268E-03
  4      14.975098022       :    0.775387E-04     : 0.775387E-04
  5       0.98080303056     :    0.621992E-03     : 0.621992E-03
  6       0.000000E+00      :                     : -- FIXED --
  7       0.000000E+00      :                     : -- FIXED --
```

Table. 1. (see Table. 2.)

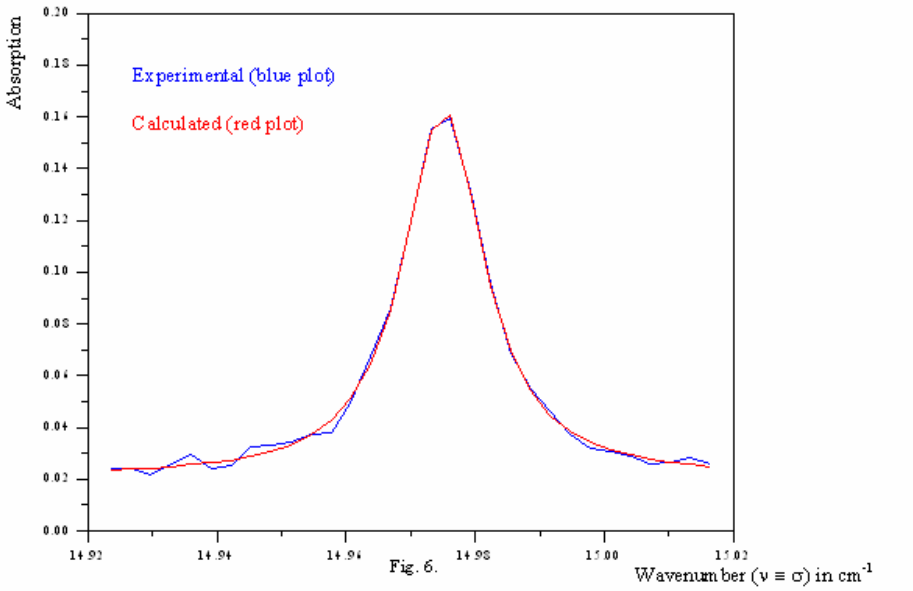

Figure 6: DUD output showing experimental and calculated single line pointed in figure 5.

PARAMETER	FITTED	STANDARD DEVIATION	STEPSIZE
1: Number of lines fitted together	1		Fixed
2: Relative Intensity $S = SoP\ell$ (cm^{-1})	0.35913745093E-02	0.613162E-04	0.613162E-04
3: Total Collisionnal Width $2\gamma_L$ (cm^{-1})	0.70768479162E-02	0.141268E-03	0.141268E-03
4: Position σ_o (cm^{-1})	14.975098022	0.775387E-04	0.775387E-04
5*	0.98080303056	0.621992E-03	0.621992E-03
6*	0.0		Fixed
7*	0.0		Fixed

Table 2: (Explanation of fit's result in Table. 1.). Converged values of parameters of the fitted line given as example. The Study Interval is 14.924 - 15.016, so $\Delta\sigma = \delta\sigma = 0.092$ cm^{-1}, RMS = $0.19152\times10^{-2} = 1.915 \times 10^{-3}$. The continuous background is $T_b(\sigma) = P(5) + P(6)\ \sigma + P(7)\ \sigma^2 = P(5) \approx 0.981 \approx 1$

- Note: In DUD, the relative intensity $S_0P\ell$ is given in cm^{-1} unit. In FitMas, the absolute intensity S_0 is given in cm. $molecule^{-1}$ converted to 296.0 K. We use the following formula [24] for conversion :

$$S_0(cm^{-2}.atm^{-1}) \text{ at } T = S_0(cm.molecule^{-1}) \times \frac{7.3391}{T} \times 10^{21}$$

$$S_0(DUD) = S_0(FitMAS) \times \frac{7.3391}{296.26} \times 10^{21}$$

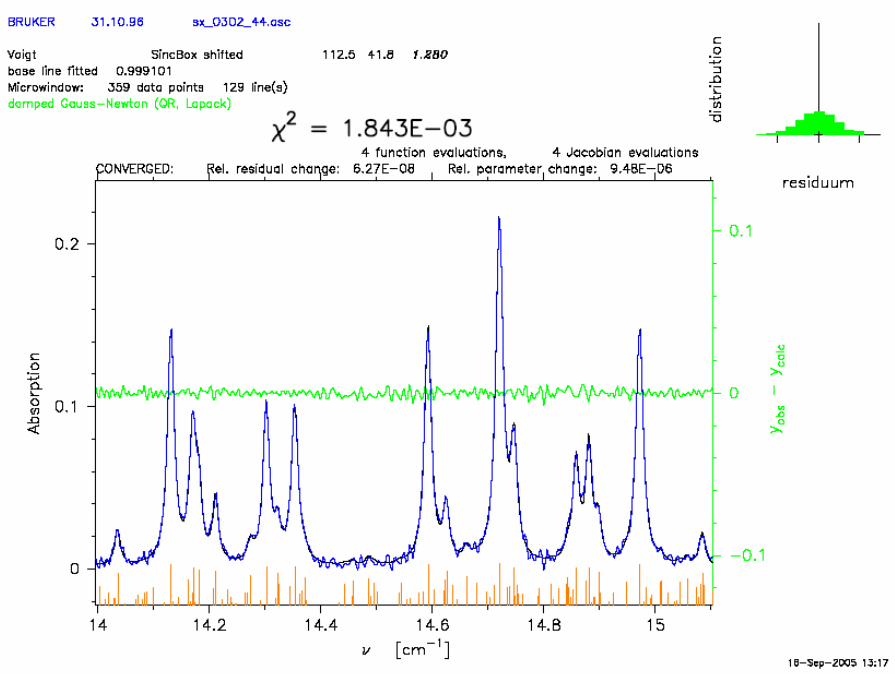

Figure 7: FitMas output showing experimental and fitted lines in a chosen spectral window. The green sticks are guessed (initial) parameters from Hitran database [8] .

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	296.3 ± 0.0	given 6.4 ± 0.0	418.0 ± 0.2

Table 3 : Experimental conditions.

Line	MW Transition [26] $\|v_1, v_2, v_3, J, K_a, K_c\rangle$	FitMas $cm.molecule^{-1}$ at 296 K.	FitMas $10^{-3}\times$ $cm^{-2}.atm^{-1}$ at 296.26 K	DUD $10^{-3}\times$ $cm^{-2}.atm^{-1}$ at 296.26 K
14.972908	000 14 2 12 → 000 14 3 11	1.740×10^{-22}	4.31	4.18
15.257700	000 12 2 10 → 000 12 3 9	1.630×10^{-22}	4.04	4.10
16.256147	000 17 2 16 → 000 17 3 15	1.892×10^{-22}	4.68	4.89
17.821559	000 25 1 25 → 000 25 2 24	1.027×10^{-22}	2.54	2.49
17.876500	000 28 0 28 → 000 28 1 27	7.596×10^{-23}	1.88	1.83

Table 4: Comparison between some absolute intensities obtained by DUD and by FitMas.

7. Conclusion

In this work, we have discussed the importance of taking into account the influence of instrumental effects. We have shown ILS' formulae used in DUD and in FitMas while considering the limited optical path difference, the finite entrance and the phase error of the Michelson type interferometer.

We have successfully compared some line intensities retrieved from pure Ozone rotational spectrum.

DUD has to be updated to have graphical facilities and to run under Linux platform rather than windows only.

Methods used by FitMas and DUD could help to obtain precise parameters in order to treat molecular spectra for many purposes, and especially for terrestrial and extraterrestrial atmospheric ones.

Acknowledgements

Acknoledgement is sincerely made by all authors to DFG-Germany and CNR-Morocco for the financial and logistic supports.

The co-author M. Badaoui is thankful, for the appreciate cooperation and help, to T. Trautmann, P. Haschberger, F. Schreier, G. Wagner and M. Birk from Remote Sensing Technology Institute of German Aerospace center (DLR) in Wessling.

The co-author M. Badaoui is grateful to V. Dana , J.-Y. Mandin and J.-M. Flaud who kindly made available many source codes and numerous documents during his Doctorat thesis in their group in LPMA Laboratory in Paris [23].

References

[1] F. Schreier, B. Schimpf, 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

[2] G. Wagner, M. Birk, F. Shreier, J. –M. Flaud, Spectroscopic database for ozone in the fundamental spectral regions, J. Geophys. Res. 107 (D22):4626, doi: 10.1029/2001JD000818 2002 (ACH – 10-1 -10-18).

[3] J. E. Dennis, R. B. Schnabel, Numerical Methods for Unconstrained Optimization and linear Equations. Prentice-Hall, (1983).

[4] P. L. Varghese, R. K. Hanson, Collisional narrowing effects on spectral line shapes measured at high resolution. App. Opt., 23 (1984) 2376-2385.

[5] 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).

[6] F. Schreier, the Voigt and Complex Error Function: A Comparison of Computational Methods. J. Quant. Spectros. Radiat. Transfer. 48 (1992) 743.

[7] J. W. C. Johns, F. Schreier, B. Schimpf, M. Birk, analysis of High-Resolution Fourier Transform Molecular Spectra. in The Future of Spectroscopy: From Astrophysics to Biology, Quebec, September 1994

[8] L. S. Rothman et al. (31 authors), J. Quant. Spectrosc. & radiat. Transfer. 82 (2003) 5-44.

[9] H. M. Pickett, R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson, H. S. P. Müller. Submillimeter, millimeter, and microwave spectral line catalog. J. Quant. Spectrosc. & Radiat. Transfer. 60 (1998) 883-890.

[10] Mary L. Ralston and Robert I. Jemrich, Technometrics, 20, No 1, February 1978.

[11] B. H. Armstrong, J. Q. S. R. T., 7 (1967) 61.

[12] W. Gautschi, Com. ACM, 12 (1969) 635.

[13] W. Gautshi, SIAM J. Numer. Anal., 7 (1970) 187.

[14] K. S. Kölbig, Com. ACM, 15 (1972) 465.

[15] G. N. Plass et D. I. Fivel, ApJ, 1(1953) 117.

[16] A. Klim, J. Quant. Spectrosc. Radiat. Transfer, 26, No 6 (1981) 537-545.

[17] N. Lacome, A. Levy, C. Boulet, J. P. Houdeau, Applied Optics, 21, No.14, 15 July 1982.

[18] J. Connes, Le journad de Physique et le Radium, Tome19 (1958) 197.

[19] H. Delouis, ''Thèse de 3ème Cycle'', Université de Paris VI (1968).

[20] H. Delouis, ''Thèse d'Etat'', Université de Paris-Sud (1973).

[21] V. Dana, J.-Y. Mandin, C. Camy-Peyret, J.-M. Flaud, J.-P. Chevillard, R.L. Hawkins, J.-P. Delfau, Appl. Opt. 31 (1992) 1928.

[22] G. Guelachvili, Distorsions in Fourier Spectra and diagnosis, in: Spectrometric Techniques, Vol. II, G.A. Vanasse (ed.), (1981).

[23] M. Badaoui, ''Thèse de Doctorat'', Université de Paris VI (1993).

[24] 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).

[25] V.A. Boldyrev and K.P. Vasilevskii, Intensity and half width of CO_2 lines in $14^01\text{-}00^00$ band, Opt. Spectrosc. 35 (1973) 476.

[26] N. Semen Mikhailenko, Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk, private communication.