Spectral shape modeling and spectra analysis for laboratory and atmospheric measurements

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Introduction: Atmospheric retrievals

Measured spectra (satellite, balloon, ground, …)

Radiative transfer
Forward model

Input spectroscopic data (Position, Intensity, spectral shape, …)

- P, T profiles
- Molecule mole fraction profiles
- Cloud altitude, aerosol
- etc. …

Spectral shapes → Collisional (pressure) effects on the spectral shape
Introduction: isolated lines and closely spaced lines

ACE spectra at different tangent altitudes

Bernath et al., GRL, 32, L15S01 (2005)
The Voigt profile
The absorption coefficient is given by

\[ \alpha_{fi}(\sigma) = S_{fi} I_{fi}(\sigma - \sigma_{fi}) \]

→ Line intensity is distributed around the line position

\[ S_{fi} = \int_{\sigma_{fi}-\Delta}^{\sigma_{fi}+\Delta} d\sigma \alpha_{fi}(\sigma) \approx \int_{-\infty}^{+\infty} d\sigma \alpha_{fi}(\sigma) \]

→ Normalized line profile \( I_{fi}(\sigma) \)

\[ \int_{-\Delta\sigma}^{+\Delta\sigma} d\sigma \quad I_{fi}(\sigma) \approx \int_{-\infty}^{+\infty} d\sigma \quad I_{fi}(\sigma) = 1 \]
The Doppler broadening

A molecule having a speed $v\neq 0$, absorbs or emits at a wavenumber $\sigma$, which is different of $\sigma_{fi}$ of this molecule at $v=0$.

The corresponding Doppler shift is: $\sigma = \sigma_{fi} \left(1 + \frac{v_z}{c}\right)$ where $v_z$ the radiator velocity component along the wave propagation vector.

The line profile is a Gaussian profile

$$I_D(\sigma - \sigma_{fi}) = \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\Delta \sigma_D} \exp\left(-\ln 2 \left[\frac{\sigma - \sigma_{fi}}{\Delta \sigma_D}\right]^2\right)$$

where $\Delta \sigma_D = \left[\frac{2k_B T}{mc^2 \ln 2}\right]^{\frac{1}{2}} \sigma_{fi}$ is the HWHM of the line.
The Lorentz broadening and shifting

For an isolated transition, the **main** effects of intermolecular collisions (pressure) are the (Lorentz) broadening and shifting of the line

\[
\Delta \propto \text{# of coll (dens or P)}
\]

\[
I_L(\sigma - \sigma_{fi}) = \frac{1}{\pi} \frac{\Gamma_{fi}}{\left(\sigma - \sigma_{fi} - \Delta_{fi}\right)^2 + \Gamma_{fi}^2}
\]
The Voigt profile

Let’s consider a speed class: \([\left( v_z \right) - \left( v_z + dv_z \right)]\) the corresponding spectral domain is \([\left( \sigma' \right) - \left( \sigma' + d\sigma' \right)]\), with \( \sigma' = \sigma_0 (1 + v_z / c) \)

Due to collisions, the spectral intensity \( I_D(\sigma' - \sigma_{fl})d\sigma' \) is redistributed as a Lorentz profile centered at \( \sigma' \). The final contribution of this speed class at \( \sigma \) is thus:

\[
I_D(\sigma' - \sigma_{fl}) d\sigma' I_L(\sigma' - \sigma')
\]

The resulting profile is then obtained by summing over all speed classes (or all \( \sigma' \)):

\[
I_V(\sigma - \sigma_{fl}) = \int_{-\infty}^{+\infty} d\sigma' I_D(\sigma' - \sigma_{fl}) I_L(\sigma - \sigma')
\]

The Voigt profile is thus a convolution of a Gaussian profile (Doppler effect) and a Lorentzian profile (collisional effect).
The Gaussian, Lorentzian and Voigt profiles

Usual behavior of the line width

![Graph showing the linewidth dependence of HF absorption line on pressure.]

- Collisions Lorentzian
- Doppler+Collision Voigt
- Doppler Gaussian
The Gaussian, Lorentzian and Voigt profiles

Comparaison between the Gaussian, the Lorentz and the Voigt profiles.

FTS ground-based absorption spectrum (CO$_2$)

Courtesy of S. Payan
Non-isolated transitions: Line-mixing effects
In some cases, for closely spaced lines, the Voigt profile fails when P increases. It predicts shapes that are too broad.

Collisions induce transfers of populations between the levels of the two lines that lead to transfers of intensity between the lines.
Line-mixing effects: Absorption coefficient

\[
\alpha^{LM}(\sigma) \propto \sum_{\text{line } \ell} \sum_{\text{line } k} \rho_k d_k \langle k \mid [\Sigma - L_0 - iPW]^{-1} \mid \ell \rangle
\]

\(\rho_k\) populations
\(d_k\) matrix element of radiation-matter coupling tensor
\(\Sigma, L_0\) matrix of positions
\(W\) relaxation operator. All effects of collisions. Independent of \(\sigma\) within the impact approximation (not too far in the wings)

\(W_{lk} \neq 0 \rightarrow\) Line coupling between \(|k\rangle\) and \(|l\rangle\)

\(W_{lk} = 0 \rightarrow\) No line coupling (Lorentz)
For moderate line overlapping, a first order perturbation approach is possible. Then we only need to know one coupling parameter \((Y, \text{related to the W matrix elements})\) per line:

\[
Y_k = 2 \sum_{\ell \neq k} \frac{d_\ell}{d_k} \frac{W_{k\ell}}{\sigma_k - \sigma_\ell}
\]
Nadir looking instruments onboard satellites
Greenhouse gases Observation SATellite (GOSAT-2, in orbit)
Orbiting Carbon Observatory (OCO-2, NASA, in orbit)
MicroCarb (CNES, under study)

Spectral regions and aims
- CO₂ from 1.6 μm (weak) and 2.1 μm (strong) bands
- Air mass from O₂ A band (0.76 μm)
- CH₄ from 2v₃ band (near 1.7 μm)
- aerosols from CO₂ and O₂ bands

Detection/quantifying sinks and sources (1 ppm for x_{CO₂}, 0.3 %)
→ Extreme accuracy of spectra modelling. Huge constraints on the spectroscopic data and the prediction of pressure effects (collisions and spectral-shape)
CO₂: ground-based measurements

Wrong air-mass (and time) dependences

Sza 79.9°, Park Falls, region 2.1 μm

Sza 79.9°, Park Falls, region 1.6 μm

CO₂ retrieved
O₂: Ground-based measurements

Sza 79.9°, Park Falls, A band

Wrong time (and air-mass) dependences

Sza 79.9°, Park Falls, 1.27 μm band
Line-mixing effects: Laboratory studies

**CO\textsubscript{2}/N\textsubscript{2}**

Abs. Coef \((10^2 \text{ cm}^{-1})\)

**O\textsubscript{2}/N\textsubscript{2} Λ band**

\(D\text{Tot} = 106 \text{ amagats}\)
\(T = 194\text{K}\)
Influence on retrievals: O$_2$ ground-based measurements

O$_2$ A band:
Relative errors on surface pressures retrieved from atmospheric spectra
Influence on retrievals: CO$_2$ ground-based measurements

Fits of a ground based transmission spectra in the region of the $2 \nu_1 + \nu_3$ band of CO$_2$

Significant errors on the CO$_2$ atmospheric amount.
Sinks and sources !!!
Other systems

CH$_3$Br, 500 hPa, 234 K, $v_6$ band
Isolated line
Measured and adjusted spectra using the Voigt profile.

H$_2$O/N$_2$, $v_3$ band, $1_{11,11} \leftrightarrow 10_{1,10} \ 11_{0,11} \leftrightarrow 10_{0,10}$

Limits of the Voigt profile
Limits of the Voigt profile

The Voigt profile neglects:

1. **The velocity changes induced by collisions.**

   The detailed balance:
   \[ P(\tilde{v} \rightarrow \tilde{v}') \times f_{MB}(\tilde{v}) = P(\tilde{v}' \rightarrow \tilde{v}) \times f_{MB}(\tilde{v}') \]
   → change from \( v \) to \( v' < v \) is more probable than that from \( v \) to \( v' > v \).
   → reduction of the Doppler broadening → collisional narrowing effect or Dicke narrowing effect

2. **The speed-dependences** of the collisional width \( \Gamma(v) \) and shift \( \Delta(v) \) of the line.
   This also (in general) leads to a narrowing of the line
Limits of the Voigt profile: atmospheric retrieval

*In situ* absorption spectrum of tropospheric H$_2$O recorded by balloonborne diode laser and its fit using the Voigt profile

*Durry et al, JQSRT 94, 387, 2005*
Limits of the Voigt profile: Influence on atmospheric retrievals

HF profile retrieved from ground-based absorption FTIR measurements (Jungfraujoch station) in the (1-0) R(1) micro-window by using the Voigt profile and the Soft Collision model, compared with the HALOE (Halogen Occultation Experiment) profiles smoothed.

Barret et al, JQSRT 95, 499, 2005
Widely used non-Voigt approaches
Simple non-Voigt approaches: the velocity changes effect

The Galatry (soft collisions, SC) profile:
- Assumes that radiators undergo only a very small changes per collision
- Introduces a velocity changing rate $v_{VC}$ related to the diffusion coefficient

The Nelkin-Ghatak (hard collisions, HC) profile:
- Assumes that velocity memory is lost after each collision
- Introduces a velocity changing rate $v_{VC}$

*We can show that the SC model is more appropriate for systems for which the active molecule is much heavier than the perturber.*

*However, experiences show that the SC and HC models lead to similar quality in term of residual fit of measured spectra*
Simple non-Voigt approaches: the velocity changes effect
Velocity changes effects: Remaining problems

Pressure dependence of the frequency optical collisions obtained for the R(24) line of CO$_2$ in air from the NGP, GP and single-spectrum fits. The green line is the frequency of optical collisions calculated from the mass diffusion coefficient.

*The collisional narrowing parameter is non linear with pressure*
Simple non-Voigt approaches: the speed dependences

- The polynomial dependence of Berman-Pickett

\[ \Gamma(v_r) \propto v_r^p \]

\[ \Gamma(v_a) = \int \Gamma(v_r).f(v_r|v_a)dv_r \]

- The quadratic dependence of Rohart

\[ \Gamma(v_a) = \Gamma_0 + \Gamma_2[(v_a/\bar{v})^2 - 3/2] \text{with } \Gamma_0 = \langle \Gamma(v_a) \rangle_{v_a} \]

\( m_{\text{active}} \gg m_{\text{buffer}} \)

Weak speed dependence

\( v_a << v_r \# v_b \)

\( \Gamma(v_a) \# \text{Cte} \)

\( m_{\text{active}} << m_{\text{buffer}} \)

Strong speed dependence

\( v_a \# v_r >> v_b \)

\( \Gamma(v_a) \# \Gamma(v_r) \)

Courtesy of F. Rohart
Simple non-Voigt approaches: the speed dependences

707<-606 and 717<-616 lines (at 0.83nm) of pure H₂O (left) and H₂O/air (right)

Ngo et al., JQSRT, 113, 870, 2012
Speed dependent Voigt profile: Remaining problems

$\Gamma_2/\Gamma_0$ non constant vs pressure!

Larcher et al, JQSRT, 2015
“Today” situation for line-shape study

- Thanks to the development of high resolution and S/N laboratory techniques (eg CEAS, CRDS) and spectra analysis techniques (multispectrum fits) the vast majority of experimental studies now clearly evidence the limits of the Voigt. Various fitting line shapes are used, chosen according to ad hoc criteria, so that the available data are inconsistent with no consensus.

- Very ambitious and precision-demanding remote sensing experiments are operational, under study or being developed (GOSAT, OCO, CarbonSat, MERLIN, Micro Carb) which require an accuracy of spectra simulations (<0.3%) that prohibits the use of the Voigt profile.
A functional form for non-Voigt line shapes for spectroscopic databases and applications
Requirements for the proposed line-shape

**Urgent need** for a **better isolated line shape** model and associated data to fit experimental/calculated spectra and feed databases used for remote sensing. This line shape should fulfill various constraints:

1- **Take into account** the various processes that affect the line profile (Doppler, molecule velocity changes, speed dependences of broadening and shifting) and be sufficiently physically-based to describe the (experimental) line profiles of **various transitions** of **various gases** with an **accuracy (<0.1%) fulfilling** the remote sensing accuracy needs

2- Be **based on well identified line-by-line parameters** with **known and physically based pressure dependences** for storage in databases

3- **Contain simpler models** as limiting cases in order to maximize the possibility to use previously published results obtained using simpler profiles

4- Require **CPU time compatible** with a **use in atmospheric spectra calculations** (many lines and layers).

5- Be **compatible** with a treatment of **line-mixing**
The Hartmann-Tran (HT) profile

→ The HT profile takes into account

- The collision-induced velocity changes (Dicke narrowing, hard collision model): $v_{VC}$
- The speed dependences of the collisional line width and shift (quadratic model): $\Delta_2, \Gamma_2$
- The correlation between velocity- and internal-state-changes: $\eta$

$\text{HTp}(\Gamma_0, \Gamma_2, \Delta_0, \Delta_2, v_{VC}, \eta)$

→ The functional form of the model can be expressed as a combination of the Voigt functions →

the HT profile can be calculated as quickly as the Voigt profile
The limits of the HT profile correspond to simplified line-shape models → parameters obtained with these models can be used with the HT profile with the appropriated parameters set to zero.

<table>
<thead>
<tr>
<th>Profile</th>
<th>Parameters</th>
<th>Limit of the HT profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>$\Gamma_0, \Gamma_2, \Delta_0, \Delta_2, \nu_{\text{VC}}, \eta$</td>
<td></td>
</tr>
<tr>
<td>qsdHC</td>
<td>$\Gamma_0, \Gamma_2, \Delta_0, \Delta_2, \nu_{\text{VC}}$</td>
<td>$\eta = 0$</td>
</tr>
<tr>
<td>qsdV</td>
<td>$\Gamma_0, \Gamma_2, \Delta_0, \Delta_2$</td>
<td>$\nu_{\text{VC}} = \eta = 0$</td>
</tr>
<tr>
<td>HC</td>
<td>$\Gamma_0, \Delta_0, \nu_{\text{VC}}$</td>
<td>$\eta = \Delta_2 = \Gamma_2 = 0$</td>
</tr>
<tr>
<td>V</td>
<td>$\Gamma_0, \Delta_0$</td>
<td>$\nu_{\text{VC}} = \eta = \Delta_2 = \Gamma_2 = 0$</td>
</tr>
</tbody>
</table>
Objective: Measure methane amounts in the atmosphere

Observation method: differential absorption of gaseous methane at two laser wavelengths reflected from Earth surface

→ Measuring absorption cross-sections of methane at 1.645 μm (2ν₃ band)
Spectroscopy for MERLIN: 0.2% accuracy required!

FS-CRDS experiments
S/N ≈ 20,000
1 MHz for absolute/relative frequency

Delahaye et al., 2016
Spectroscopy for MERLIN: 0.2% accuracy required!

Delahaye et al, 2016
Validation with ground-based atmospheric spectra (TCCON)

Delahaye et al, 2019
Summary

• Spectral shape has become a key issue for high precision soundings (e.g. greenhouse gases)

• When line is isolated, the Voigt profile fails to model isolated line-shape, velocity effects should be taken into account

• When lines are closely spaced, line-mixing should be taken into account

• Increasing evidences of influence of refined spectral shape effects for remote sensing

• Need to take into account both line-mixing and velocity effects; through the HT profile
  -> profile recommended by IUPAC and adopted by the HITRAN spectroscopic database
For more details