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Multi-spectrum fitting software for advanced spectral line shapes analysis

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Multi-spectrum fitting software for advanced spectral line shapes analysis

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Abstract. We present a multi-spectrum fitting software that enables advanced analysis of high-resolution atomic and molecular spectra in a large range of pressures. Individual lines are modeled with theoretical profiles that take into account the non-Voigt line shape effects, such as the speed-dependence of collisional broadening and shift, velocity-changing collisions and their correlations with phase/state changing collisions, first order line mixing and collision-time asymmetry.

1. Introduction

Increasing requirements for high-accuracy spectroscopic data has led to a transition from the commonly used Voigt profile to more advanced and physically justified line-shape models in spectroscopic databases, reference laboratories and high-precision remote sensing applications. As shown in many papers, e.g. [1, 2, 3], a sub-percent agreement of experimental data with the fitted line shape in typical atmospheric conditions requires taking into account such physical effects as: speed-dependence of collisional broadening and shift [5], velocity-changing collisions, which leads to Dicke-narrowing [4] and their correlations with phase/state changing collisions [6]. For non-isolated lines, line mixing [7] may also play an important role. In semiclassical line shape theory these effects may be described using the correlated asymmetric speed-dependent Rautian-Sobelman profile (CSDARSP) [8, 9] and its simplifications, such as the Hartmann-Tran profile (HTP), recently recommended as a standard line-shape model to replace the Voigt profile in spectroscopic databases [2, 10], e.g in HITRAN [11, 12]. In real experimental conditions, where the spectra have finite signal-to-noise ratio, numerical correlations between some line-shape parameters make data fitting difficult. In such cases a multi-spectrum fitting approach [13] is used. In this approach shared line parameters are fitted to a set of spectra measured at different gas pressures, which makes it possible to obtain a set of line parameters consistent in a wide range of gas pressures.

2. Software capabilities

Our spectra fitting software consists of two main components. A Fortran-based library contains an implementation of the Levenberg-Marquardt nonlinear least-squares fitting algorithm [14] and algorithm that defines a theoretical model describing a set of fitted spectra. A LabView-based interface enables convenient reading of experimental spectra, setting the line-shape model

and initial parameters of spectral lines, provides a tool for graphical representation of the data and fit, and finally saving the fit results.

The Fortran-based library, compiled to a DLL file, provides access to functions which fit the user provided multi-spectrum data with a chosen model. The individual line shapes can be modeled with simplifications of CSDARSP. Speed-dependent effects can either be modeled with the quadratic [15] or hypergeometric approximation [5], while velocity-changing collisions are modeled within the soft- or hard-collision approximation. The correlation between velocity-changing and phase/state changing collisions can be modeled by one of two common approaches, i.e. the speed-independent complex parameter of frequency of optical collisions [9] or the speed-dependent correlation parameter, typically denoted as η [1], used also in HTP. The first order line mixing effects [16] can be modeled by additional pressure-dependent parameters, which may also describe collision-time asymmetry [17]. The relative accuracy of numerical calculations of the line shape functions, mostly limited by the numerical accuracy of the integration methods used, was tested to be at least 10^{-6}. The experimental spectra can be provided in a form of an absorption coefficient, a cavity ring-down time constant or a transmission through absorption cell or optical cavity, according to Lambert-Beer law. Instrumental features of a spectrum, such as a linear background and the etalon fringes, can be fitted together with line shapes.

The LabView-based program, partially shown in Fig. 1, provides a convenient user interface for spectra fitting. Each of the initial parameters of the single- or multi-spectrum fitting model can be set as individual for each pressure or a shared parameter for all pressures, with either a
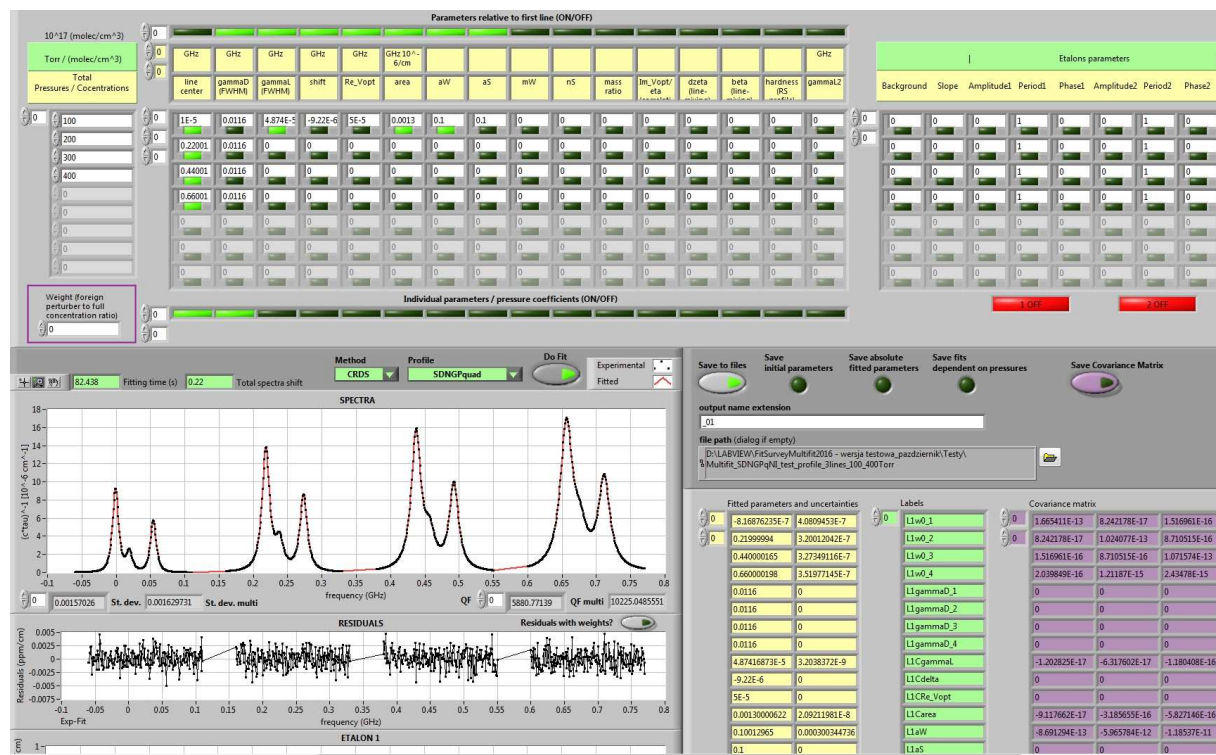

Figure 1. The main part of the LabView-based program interface. The upper part enables settings of gas pressures and initial parameters of the model. Graphs in the lower part represent a multi-spectrum fit of example spectrum of 3 lines, measured at 4 pressures. The lower graph represents fit residuals. In the lower right part a list of fitted parameters with uncertainties and covariance matrix are displayed.

linear pressure dependence (e.g. collisional broadening) or pressure independent (e.g. Doppler broadening). For convenience, in the case of multi-line spectra the parameters can be optionally set as relative to the corresponding parameters of a reference line (e.g. to the strongest line). The output files contain the experimental and fitted spectra and their differences, the fitted parameters of the model with standard uncertainties, the quality of the fit (QF) parameter [18, 19] and optionally the covariance matrix of the fitted parameters.

3. Conclusions

Our multi-spectrum line-shape fitting software enables analysis of high-precision spectra with advanced semi-classical models. So far this software, or its earlier versions, were used to analyze cavity ring-down spectra of O_2 [20, 21], CO [22, 23], CO_2 [19, 24] and H_2O [3, 25]. It was also used in analysis of the O_2 [26, 27], CO [28] and D_2 [29] data, presented as posters at the ICSLS 23 conference.

In the future we plan to extend the program functionality by adding temperature dependencies of line parameters in the multi-spectrum fitting to enable analysis of pressure and temperature dependencies of spectra and fitting temperature dependencies of line-shape parameters. We also plan to extend a list of available line profiles by adding a combination of hard- and soft-collision for velocity-changing collisions.

References

[1] Pine A S 1999 *J. Quant. Spectrosc. Radiat. Tr.* **62** 397
[2] Ngo N H *et al* 2013 *J. Quant. Spectrosc. Radiat. Tr.* **129** 89
[3] Lisak D *et al J. Quant. Spectrosc. Radiat. Tr.* **164** 221
[4] Dicke R H 1953 *Phys. Rev.* **89** 472
[5] Berman P R 1972 *J. Quant. Spectrosc. Radiat. Tr.* **12** 1331
[6] Rautian S G, Sobelman I I 1967 Sov. Phys. Usp. **9** 701
[7] Baranger M 1958 *Phys. Rev.* **111**, 481
[8] Lance B, Robert D, 1999 J. Chem. Phys. **111** 789
[9] Ciuryło R, Pine A S, Szudy J 2001 *J. Quant. Spectrosc. Radiat. Tr.* **68** 257
[10] Tennyson J *et al* 2014 Pure Appl. Chem. **86** 931
[11] Kochanov R V *et al* 2016 *J. Quant. Spectrosc. Radiat. Tr.* **177** 15
[12] Wcisło P *et al* 2016 *J. Quant. Spectrosc. Radiat. Tr.* **177** 75
[13] Chris Benner D *et al* 1995 *J. Quant. Spectrosc. Radiat. Tr.* **53** 705
[14] Press W H *et al* Numerical Recipes in Fortran, Cambridge University Press, 1992, pp 678
[15] Rohart F *et al* 1994 *J. Chem. Phys.* **101** 6475
[16] Rosenkranz P 1975 IEEE Trans. Antennas. Propag. **23** 498
[17] Szudy J, Baylis W E, 1996 *Phys. Rep.* **266** 127
[18] Cygan A *et al* 2012 *Phys. Rev. A* **85** 022508
[19] Bui T Q *et al* 2014 *J. Chem. Phys.* **141** 174301
[20] Wójtewicz S *et al* 2015 *J. Quant. Spectrosc. Radiat. Tr.* **165** 68
[21] Domysławska J *et al* 2016 *J. Quant. Spectrosc. Radiat. Tr.* **169** 111
[22] Wójtewicz S *et al* 2013 *J. Quant. Spectrosc. Radiat. Tr.* **130** 191
[23] Cygan A *et al* 2016 *J. Chem. Phys.* **144** 214202
[24] Lin H *et al* 2015 *J. Quant. Spectrosc. Radiat. Tr.* **161** 11
[25] Sironneau V, Hodges J T 2014 *J. Quant. Spectrosc. Radiat. Tr.* **152** 1
[26] Bielska K *et al* 23rd ICSLS Book of Abstracts, Wydawnictwo Naukowe UMK, Toruń, 2016, pp 116
[27] Domysławska J *et al* 23rd ICSLS Book of Abstracts, Wydawnictwo Naukowe UMK, Toruń, 2016, pp 122
[28] Stec K *et al* 23rd ICSLS Book of Abstracts, Wydawnictwo Naukowe UMK, Toruń, 2016, pp 136
[29] Zaborowski M *et al* 23rd ICSLS Book of Abstracts, Wydawnictwo Naukowe UMK, Toruń, 2016, pp 149