Program RELIP for photo-acoustic data analysis

Mikhail Yu. Kataev and Olga Yu. Nikiforova

Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences
Akademicheskii Ave. 1, 634055, Tomsk, Russia
e-mail: kataev@mail.tomsknet.ru, nik@asd.iao.ru

The RELIP (Retrieving Line Parameters) software for photo-acoustic (PA)-spectroscopy data processing is developed in the Laboratory of Atmospheric Absorption Spectroscopy of the Institute of Atmospheric Optics SB RAS. This software is developed for reconstruction of line centers and halfwidths from experimental absorption spectra. Doppler, Voigt, and Lorentz line contours are used in the fitting procedure. It is possible to reconstruct simultaneously the above-mentioned parameters for several absorption lines. The experimental data of a special form such as frequency derivative of the PA signal are acceptable. There is an additional option aimed to compensate for the background of a signal. The software provides the graphical presentation of the measurement data and fitting results together with the tables. The experimental data on the PA signal and the PA signal derivative for the absorption bands of H2O lying near 0.69 \( \mu \text{m} \) and 0.59 \( \mu \text{m} \) as well as the model calculations are used at the software testing.

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In connection with development of computer facilities in the last years, means for processing of experimental data, such as specialized software packages for processing of experimental results, become more visual and permit conducting multivariate analysis of data for optimal choice of a processing technique in each specific case. Software packages applicable for processing of spectroscopic information can conditionally be divided into two groups: universal and specialized ones (developed for specific device and experimental or processing technique). Universal packages include the following: ORIGIN (with the PeakFit program), OPUS/LT (Bruker Corporation), GRAMS/32 (GALACTIC Corporation), PEAKSOLVE, FOCUS, OMNIC (NICOLET Corporation), IPLAB (Scanalytic Corporation), SCARP (PERKIN ELMER Corporation), WINFIRST (MATTSONIR Corporation).\(^7\)–\(^10\) Among the specialized software packages are such as INTBAT,\(^1,2\) OPTIMIZE,\(^5\) DECOMP,\(^3,4\) FITMAS,\(^6\) and others. The packages of both categories allow one to extract the information on parameters of separate lines from experimentally recorded transmission spectra, to make some manipulations with a spectrum, to conduct decomposition of complex contours into separate components, to compare experimental results with model ones calculated using their own databases of spectroscopic parameters of absorption lines or from the HITRAN database. However, the above-mentioned packages are badly adapted to processing of the results of the photo-acoustic (PA) measurements, because they do not take into account such features of the PA method as the proportionality of a registered signal directly to absorption (instead of transmittance), representation of observational data in arbitrary units, and availability of a background signal of various nature.

The RELIP (Retrieval Line Parameters) software package described in this paper has been developed as a result of processing of the data of photo-acoustic measurements in order to extract the spectroscopic information.\(^11,12\) This software allows one to solve the following problems: 1) gathering and storage of observational data and line parameters obtained in processing; 2) preliminary processing of observational data (smoothing, separation out of a base line, centering, etc.); 3) data processing by the methods of nonlinear optimization or random search to retrieve the parameters of lines; 4) graphic and tabular representation of measurement data and processing results. Retrieved parameters in the RELIP software are the position of the line centers, their Lorentz halfwidths and intensities. This software package has been developed in the environment of DELPHI–3 visual programming and on the basis of modern version of FORTRAN PS–4 numerical language; it requires the Windows 95–98, NT operating system.

Structure and options of RELIP software

The basic structure elements of the software and their functions are shown in Fig. 1.

[Diagram of RELIP software structure]

Fig 1. The basic structure elements of RELIP software and their functions.
The package is oriented at the input file, in the dat format, consisting of two columns of numbers. The first column relates to the frequency (or wavelength; arbitrary units are possible), and the second one relates to the recorded PA signal (also in arbitrary units). The file can be subsequently saved (together with the obtained results) in the internal database of the RELIP package for further usage of these data at processing of subsequent realizations of a spectrum.

When reading the file it is necessary to indicate the type of measurement (PA signal or its derivative) and the type of contour of the absorption line for fitting: Doppler (1), Lorentz (2) or Voigt (3):

\[
f(v) = \frac{S}{\gamma D} \ln \frac{v - v_0}{\gamma D}, \quad K_0 = \frac{S}{\gamma D} \ln \frac{v - v_0}{\gamma D},
\]

Here \( S, \gamma, \gamma D, \) and \( v_0 \) are the parameters of an absorption line: intensity, Lorentz and Doppler profile halfwidth, and frequency of the line center, respectively; \( m \) is the weight of a molecule; \( T \) is the gas temperature, in K; \( c \) is the speed of light, and \( k \) is the Boltzmann constant. Let us note that when fitting a model contour to experimental results the fitted parameters are \( v_0, \gamma, \) and \( U \) (amplitude of the registered signal), while the intensity of a line is determined at the final stage by integration of a model contour with amplitude \( U \) in the range \( v_0 \pm 5\gamma \).

Additional capability at reading of a data file is allocation of a range for processing and analysis, for example, if an experimental record contains too many absorption lines or some region of a spectrum should be investigated in more detail. The following stage, if necessary, is the pretreatment of the data. It enables to sort the data by frequency, to average repeated data (or to fill the incomplete data), by passing to a homogeneous frequency grid. The data can be differentiated or integrated.

Many experimental data contain the background component of either physical or instrumental nature. The correct determination of background is rather essential when determining a halfwidth (and intensity). To be eliminated, the background is determined either as a constant, the linear function of readouts \( y(x) = ax + b \) (where coefficients of model are easily determined from the equations \( a = (y_N - y_1)/(x_N - x_1) \) and \( b = y_1 - ax_1 \), \( N \) is the number of measurements selected for processing), or as a quadratic model of the background like \( y(x) = a_1 + a_2 x + a_3 x^2 \), the coefficients of which can be found from solution of the system of linear algebraic equations \( a = (A^T A)^{-1} A b \), where \( a = (a_1, a_2, a_3) \), \( y = (y_1, y_2, y_N) \) and \( A \) is the matrix.
In some cases, there is a necessity of smoothing the measurements (elimination of random component), that can result in the increase in accuracy of reconstructed parameters. The package also includes the procedures of smoothing by different methods: spline-functions, Fourier and median filter (by chosen necessary points for smoothing window).

When working with the data of measurements, sometimes we need to change their presentation a little, for example, to change a scale along one or both axes, etc. For this purpose the RELIP package includes the specialized calculator (DataCalc), which allows one to multiply, divide, add, and subtract numbers both from the measurements scale and functional dependence (see Fig. 2). Besides, for operation with individual elements the package includes a usual engineering calculator. This all makes the processing and analysis of the observed data more visual.

The next step in processing is selection of an initial approximation. In principle, it is possible, based on the plot shown on the screen, to set the number of lines and their parameters manually, directly typing values from the keyboard in the corresponding cells of the database table (option «Parameters of lines» in the bottom of the screen). However, if the spectrum contains a large number of lines or lines are hardly overlapping, it is worth using the special means available in the «Analysis» menu. Thus the retrieved values fill the database table, and when using the option «Simulations» the model line corresponding to the calculation by parameters of the table appears on the plot together with the experimental data (Fig. 3).

We have realized a flexible system of storage of the processed values (in contrast to the available analogs); this system allows one to relate the data to the selected data. It is useful in that case, when the same sequence of the data is processed several times, what allows comparison of these results.

The accuracy of the retrieved parameters can be controlled
by checking the discrepancy between a model curve (determined from the retrieved parameters) and the measurement data. The important advantage of the RELIP software is the availability of an option of calculation of the probability density from the discrepancy. It is known that the probability density of a random component should correspond to the normal law. The difference of the determined probability distribution from the normal law allows one to control the observed data and to draw a conclusion on availability of some systematic component in measurements, incorrectly selected model, or others.

Option «Fourier» serves for investigation of spectral components of the model curve. The numerical results of data processing are graphically displayed in separate windows and option «Additional» permits setting the previous model curve in the lower part of the screen to compare the results of different processing methods. The user can save the data as a new file, change the view of a plot, and print it out.

It should be noted in conclusion that the architecture of the RELIP software package allows its functional capabilities to be further extended and new algorithms for data processing to be implemented.

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