RELIP software and its application to determination of spectral line parameters from photoacoustic measurement data

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Received December 4, 2000

RELIP software package is developed for determining parameters of absorption lines from the data of photoacoustic measurements of an absorption spectrum or its frequency derivative. The functionality of the package is described as applied to pre-processing of experimental data, reconstruction of spectral line parameters, and analysis of results.

The photoacoustic (PA) method of recording spectra is often used in solving spectroscopic problems.[1–3] The results of PA measurements are then processed in order to find the parameters of a spectral line profile. For this purpose, versatile software packages for IBM-compatible personal computers can be applied, such as ORIGIN (with PeakFit program), OPUS/LT (Bruker), GRAMS/32 (GALACTIC), PEAKSOLVE, FOCAS, OMNIC (NICOLET), IPLAB (Scanalytic), SCARP (PERKIN ELMER), and WINFIRST (MATTSONIR).[4–7] There exist also a number of specialized software packages for obtaining spectral information, such as INTBAT,[8] OPTIMIZE,[9] DECOMP,[10,11] and FITMAS.[12] However, the versatile packages ignore the peculiarities of the used measurement technique, and the purpose of most specialized packages is a processing of transmission spectra. Therefore we have developed a specialized software package RELIP (Retrieval of Line Parameters) for determining halfwidths and centers of absorption lines from the results of PA measurements, as well as for accumulation and analysis of the obtained information.[13]

Mathematical background

The spectrum of some PA signal $A(\nu)$ to be detected can be presented as a convolution of the spectral dependence of the absorption coefficient of a gas (or a mixture of gases), filling the PA cell, $k(\nu)$ and the spectrum of exciting radiation $g(\nu)$ (Ref. 14):

$$A(\nu) = \int g(\nu - \nu')\, k(\nu')\, d\nu' + \beta(\nu),$$

where $\beta(\nu)$ is the background component, which is usually present in the measured signal.

If the width of the exciting radiation spectrum is negligibly small in comparison with the width of an absorption line, then the relation between the recorded signal and the spectrum under study is linear:

$$A(\nu) \sim I_0\, k(\nu) + \beta(\nu).$$

This is one of advantages of the PA method.[15] A disadvantage of the PA method is a presence of the background β, which can be caused by radiation absorption due to interfering gases in the cell, cell windows, and many other factors.[15] Therefore, the background can have both selective and non-selective character. To exclude the contribution due to the non-selective component, sometimes the frequency derivative of the PA signal is recorded rather than the signal itself.[16] In this case, the recorded signal is related to the spectrum under study as:

$$A'(\nu) = C\, \frac{\partial k(\nu)}{\partial \nu}\,.$$

RELIP provides a means for processing both the PA signal and its derivative.

The procedure of processing measurement results can be conditionally subdivided into three stages: pre-processing, fitting the chosen model function, and analysis.

Pre-processing of a recorded spectrum includes:

(a) changing by a constant (addition and/or subtraction, multiplication and/or division) along a horizontal or vertical axis and centering by equations

$$\overline{A}_i = A_i - \langle A \rangle; \quad \langle A \rangle = \frac{1}{N} \sum_{i=1}^{N} A_i,$$

for example, for reducing the spectrum to a convenient scale along the axes;

(b) taking the logarithm or exponent and integrating or differentiating for comparison of spectra, obtained by different methods, with, for example, transmission data;

(c) smoothing for removal of the random component due to measurement noise in the recorded spectrum (using a moving average, Fourier or median filter, or splines[17]);

(d) removing repetition and interpolating to reduce the spectrum to a uniform frequency grid, to reduce the number of points to a given number, or to obtain an ordered (increasing or decreasing) frequency series;

0235-6880/01/01 44-04 $02.00

(e) correcting the base line in the form of a constant, linear or square function of frequency (for example, on the assumption of the linear frequency dependence, the background signal is calculated by the equations $\beta = a_1\nu + a_2$; $a_1 = (A_N - A_1)/(\nu_N - \nu_1)$ and $a_2 = A_1 - a_1\nu_1$ and subtracted from the recorded signal).

If the spectrum of the exciting radiation cannot be considered as a δ-function, then the recorded spectrum should be deconvolved before fitting.[18] When reconstructing the broadening and shift coefficients for H_2O absorption lines in the region of 0.59 μm from the derivative of the spectral line profile measured with a two-channel PA spectrometer with a double-frequency laser,[14] we proposed two simple algorithms of deconvolution[19] on the assumption that the spectrum can be presented as a function $g(\nu) = A_1\,\delta(\nu) + A_2\,\delta(\nu + \Delta\nu)$. However, RELIP does not include these procedures, and deconvolution should be performed beforehand by independent methods. To compare the spectra recorded with different spectral resolution, sometimes it is convenient to use the procedure of convolution of one spectrum with the instrumental function of a known (given) form.[20]

Pre-processing can give a smooth function characterizing the absorption spectrum of the gas under study. The peculiarities in the behavior of this function can be analyzed, in principle, without fitting a given (model) profile. This analysis can reveal, for example, asymmetry of lines in the spectrum of interest.

The next stage of processing is, as a rule, determination of parameters of spectral lines from fitting the chosen model line profile to the recorded spectrum.[2,21–23] RELIP uses the following types of model profiles:

(a) Doppler profile

$$k_D(\nu) = \sqrt{\ln 2}/(\gamma_D\sqrt{\pi})\,\exp(-x^2);$$

(b) Lorentz profile

$$k_L(\nu) = \frac{1}{\gamma_D\sqrt{\pi}}\,\frac{y}{y^2 + x^2};$$

(c) Voigt profile

$$k_V(\nu) = \frac{y}{\pi}\int_{-\infty}^{\infty}\frac{\exp(-t^2)\,dt}{y^2 + (x - t)^2},$$

where $x = \sqrt{\ln 2}\,(\nu - \nu_0)/\gamma_D$; $y = \sqrt{\ln 2}\,\gamma_L/\gamma_D$; ν_0 is the central frequency of an absorption line; γ_D and γ_L are Doppler and Lorentz halfwidths (HWHM) of a spectral line.

In most cases the fitting procedure requires setting the initial parameters.[9,24,25] These parameters are: the number of lines in a spectrum, their central frequencies, halfwidths, and amplitudes (and, optionally, intensities).

Since absorption lines in a recorded spectrum can overlap, their number not always is determined visually. There exist different methods for automatic counting the lines (peaks) in a spectrum. RELIP uses the most versatile method of derivatives (the second and fourth ones[26]), which allows determination of the number of lines in a spectrum and their central frequencies. Note that in this method the problem of separating overlapped or weak lines against a background of noise is still open.

To estimate halfwidths and amplitudes of the found lines and background component, we can use, for example, the equations proposed for estimating the parameters of an isolated line[17]:

$$k_0 = A_{max}\,\frac{A(\nu_1) - A(\nu_2)}{k(\nu_1) - k(\nu_2)};$$

$$\beta = A_{max}\,\frac{k(\nu_1)\,A(\nu_2) - k(\nu_2)\,A(\nu_1)}{k(\nu_1) - k(\nu_2)};$$

$$\gamma_L = \gamma\sqrt{\frac{A_{max} - 2\beta}{A_{max}}}\times$$

$$\times\left(7.7254 - 6.7254\sqrt{1 + \frac{0.3195}{\ln 2}\ln\left(1 + \frac{A_{max}}{A_{max} - 2\beta}\right)\frac{\gamma_D^2}{\gamma^2}}\right),$$

where $A(\nu)$ is the shape of the smoothed profile of the absorption line normalized to unity; A_{max} is the maximum value of the smoothed profile; $k(\nu)$ is the normalized shape of the profile of a chosen theoretical model of an absorption line; k_0 is the value of the absorption coefficient at the line center; γ is the halfwidth at the level of $0.5\,A_{max}$, and ν_1 and ν_2 are the corresponding frequencies at $A = 0.5\,A_{max}$. The proposed equation for γ_L is derived on the basis of the well-known Matveev approximation.[27]

Since the profile shape is nonlinearly related to the sought line parameters $\{p_j\}$, we chose for fitting the Levenberg–Marquardt method, widely used in solving similar problems. In this case, the parameters are determined by solving the set of equations[28]:

$$\delta\mathbf{p} = (\mathbf{B}^T\,\mathbf{W}\mathbf{B} + \alpha\mathbf{I})^{-1}\,\mathrm{B}^T\,\mathbf{W}\,\delta\mathbf{y},$$

where $\delta p_j = p_j - p_{j0}$; $\delta y_i = A_i - k(\nu_i, p_j)$, $i = 1, \ldots, N$; ν_i is the series of frequencies at which the spectrum A_i was recorded, $k(\nu_i, p_j)$ is the spectrum calculated at the same frequencies at the initial values of the parameters $\{p_{j0}\}$; $\mathbf{W}$ is the matrix of weighting factors determined by the measurement errors; $B_{ij} = \dfrac{\partial k_i}{\partial p_j}$; $\alpha > 0$ is a parameter determined by the conditions of the problem; $\mathbf{I}$ is a unit matrix. With this method, a solution can be found rather fast,[28] but at a rough initial approximation and/or high noise level the found solution may occur insufficiently accurate (i.e., to be a local minimum). Therefore, there is a possibility in

RELIP to use the random search method,[29] which is a modification of the exhaustive search method and always gives a stable solution (global minimum) in a given interval. In this case, the accuracy is determined by the step of the method. Along with the mentioned two methods, the user can search the parameters manually based on visual comparison of experimental and model spectra.

The quality of the obtained solution is analyzed by calculating the absolute discrepancy.

RELIP characteristics

RELIP functionality includes: (1) direct acquisition and storage of measurement results and line parameters obtained as a result of processing; (2) primary processing of measurement results (smoothing, determining the base line, centering, etc.); (3) processing of data by the methods of nonlinear optimization and the method of random search in order to reconstruct line parameters; (4) visualization of measurement data and processing of results in tabulated and graphic forms. The parameters to be reconstructed in RELIP are the line position, collisional halfwidth, and strength. RELIP has been developed in the DELPHI–3 environment of visual programming with the use of the current version of the language FORTRAN PS–4. RELIP operates in the operating systems Windows95–98, NT.

RELIP uses the input file in the format *dat*. This file consists of two columns of numbers, the first of them characterizes the frequency (or wavelength, possibly, in relative units), and the second one characterizes the recorded PA signal (also in relative units). The file can then be stored (together with the obtained results) in the RELIP inner database for further comparison and use of the results in processing the following realizations of the spectrum.

When fitting the model profile to the experimentally recorded one, the fitting parameters are: the position of an absorption line ν_0, its Lorentz halfwidth γ_L, and the amplitude of the recorded signal. The line strength is determined at the final stage by integrating the model profile with the obtained amplitude in the interval $\nu_0 \pm 5\gamma_L$.

RELIP can be applied to processing of both an individual spectral line and a fragment of a spectrum. However, if a fragment includes too many spectral lines, then the procedure of reconstruction takes much time, and its results are inconvenient for analysis. Therefore, there is a possibility to choose a fragment including only one or several experimental lines. Before fitting, the user can sort the data by frequency, average repeated data (or fill gaps) by going to a uniform frequency grid, and remove a non-selective component. The data can be differentiated or integrated. If necessary, the recorded spectrum can be smoothed prior to processing. For convenient graphic presentation, plots can be scaled along one or both axes, the data can be transformed using the specialized calculator (DataCalc), which allows the user to operate with the whole set of data $\{\nu_i\}$ or $\{A_i\}$ (to multiply, divide, add, and subtract). For operation with individual elements, RELIP includes an ordinary engineering calculator.

The initial approximation can be selected automatically or manually by direct input of the values from a keyboard to the corresponding cells of the database using the plot shown on the screen. The manual method is more visual, but if the processed fragment includes a large number of lines or highly overlapping lines, then the automatic method is preferable. This method determines the number of lines, and the found values automatically fill the cells in the table. As a result, the experimental plot on the screen becomes supplemented with the line representing the calculation with the tabulated parameters.

The system of storing the obtained values in RELIP allows the same set of data to be processed several times by different methods to compare the results. The fitting can be performed by the Levenberg–Marquardt method or the random search method. The former gives good results for a small number of parameters (i.e., a small number of processed lines) at a sufficiently accurate initial approximation and low noise level. The method of random search takes longer time, but it gives good results for wider range of experimental data. As the program runs, the model spectrum is graphically displayed with its parameters, presented below in a table form (see Figure 1). The processing accuracy is controlled by calculating the discrepancy. The probability density calculated from the discrepancy allows one to draw conclusions on the presence of some systematic component in measurements, on an incorrectly chosen model, or other problems in the processing. To check the RELIP efficiency in processing of results of PA measurements, halfwidths and shifts of some H_2O absorption lines were reconstructed from the experimentally recorded spectrum of a PA signal and its derivative. The obtained values agree with the earlier obtained data[14,30] accurate to the error of reconstruction. Visualization of the process of fitting and analysis makes RELIP a convenient and reliable tool for determining spectral line parameters from experimentally recorded spectra.

Acknowledgments

The authors are thankful to V.A. Kapitanov and V.V. Lazarev for experimental data kindly placed in their disposal, and A.V. Gryaznov and E.V. Zakharenko for active participation in development of the RELIP software package.

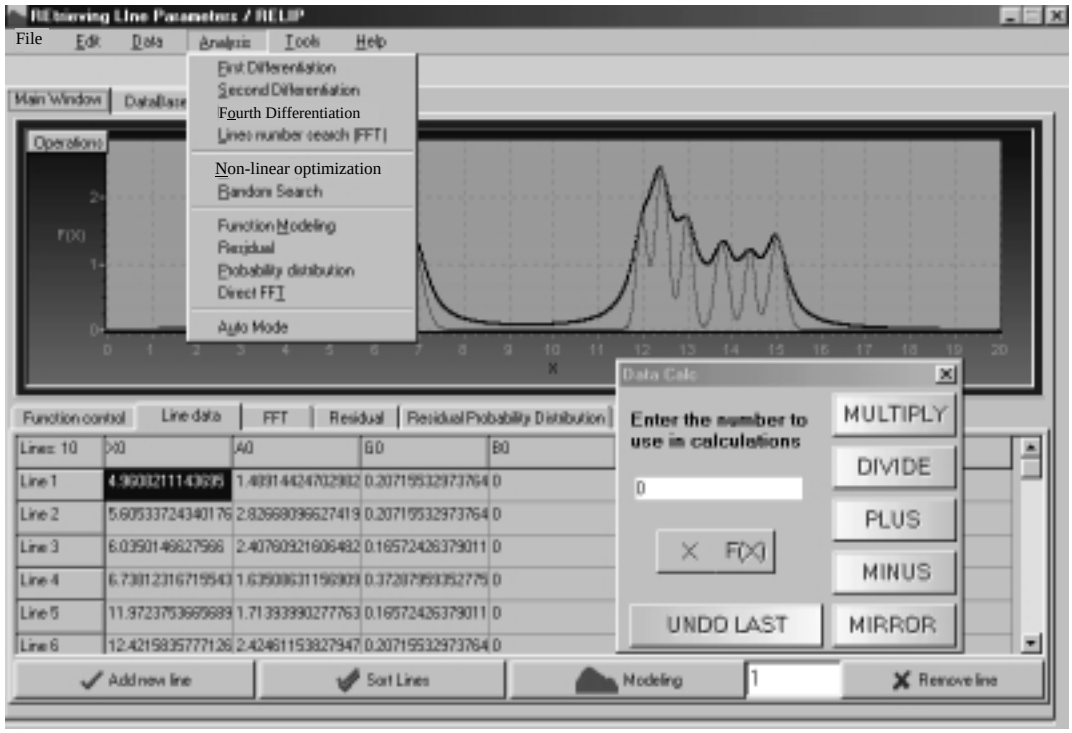

Fig. 1. User's interface of RELIP in the problem of determination of spectral line parameters from results of PA measurements.

References

1. A.B. Antipov, V.A. Kapitanov, Yu.N. Ponomarev, and V.A. Sapozhnikova, *Photo-Acoustic Method in Laser Spectroscopy of Molecular Gases* (Nauka, Novosibirsk, 1984), 128 pp.
2. V.E. Zuev, Yu.S. Makushkin, and Yu.N. Ponomarev, *Spectroscopy of the Atmosphere* (Gidrometeoizdat, Leningrad, 1987), Vol. 3, 247 pp.
3. M.Yu. Kataev and A.A. Mitsel, Preprint No. 4063–99, Dep. in Izv. Vyssh. Uchebn. Zaved., Ser. Fizika, No. 10 (1992).
4. www.nicolet.com
5. www.perkin-elmer.com
6. www.spss.com
7. www.mattsonir.com
8. J.W.C. Johns, J. Mol. Spectrosc. **125**, 442–464 (1987).
9. Y. Heyner, O. Steier, et al., J. Quant. Spectrosc. Radiat. Transfer **56**, No. 5, 769–782 (1996).
10. O.L. Polyansky, J.R. Busler, et al., J. Mol. Spectrosc. **176**, 305–315 (1996).
11. R.S. Ram and P.F. Bernath, J. Mol. Spectrosc. **176**, 329–336 (1996).
12. F. Schreier, B. Schimpf, and M. Birk, in: *Procs. of XIII Colloc. on High Res. Mol. Spectrosc.*, Riccione (1993).
13. M.Yu. Kataev and O.Yu. Nikiforova, in: *Procs. of XIII International Symposium and School on High Resolution Molecular Spectroscopy*, Tomsk (1999).
14. V.A. Kapitanov, M.Yu. Kataev, and O.Yu. Nikiforova, Atmos. Oceanic Opt. **9**, No. 7, 585–589 (1996).
15. V.P. Zharov and V.S. Letokhov, *Laser Photo-Acoustic Spectroscopy* (Nauka, Moscow, 1984), 320 pp.
16. A.D. Bykov, V.A. Kapitanov, et al., Atm. Opt. **3**, No. 2, 133–140 (1990).
17. M.Yu. Kataev, V.V. Lazarev, O.Yu. Nikiforova, and I.V. Ptashnik, in: *Abstracts of Reports at First Inter-Republic Symposium on Atmospheric and Ocean Optics*, Tomsk (1994), p. 32.
18. X. Jiyao and W. Yingjian, J. Quant. Spectrosc. Radiat. Transfer **48**, No. 4, 419–426 (1992).
19. M.Yu. Kataev, A.A. Mitsel, O.Yu. Nikiforova, and V.A. Fedorov, SPIE Proc. **3090**, 319–322 (1996).
20. H.H. Madden, Analyt. Chem. **50**, No. 9, 1383–1384 (1978).
21. V.G. Avetisov, A.N. Nadezhdinskii, A.N. Khusnutdinov, P.M. Omarova, and M.V. Zyrianov, J. Mol. Spectrosc. **160**, No. 2, 326–334 (1993).
22. B.E. Grossman and E.W. Browell, J. Mol. Spectrosc. **136**, 264–294 (1989).
23. B.E. Grossman and E.W. Browell, J. Quant. Spectrosc. Radiat. Transfer **45**, 339–348 (1991).
24. A. Premoli and M.L. Rastello, Appl. Spectr. **43**, No. 3, 539–566 (1989).
25. D.C. Benner, C.P. Rinsland, V.M. Devi , et al., J. Quant. Spectrosc. Radiat. Transfer **53**, No. 6, 705–721 (1995).
26. G. Fleissner, W. Hage, A. Hallbrucker, et al., Appl. Spectr. **50**, No. 10, 1235–1243 (1996).
27. V.S. Matveev, Zh. Prikl. Spektrosk. **16**, 228 (1972).
28. J. Dennis and R. Schnabel, *Numerical Methods of Unconditional Optimization and Solution of Nonlinear Equations* [Russian translation] (Mir, Moscow, 1988), 440 pp.
29. L.A. Rastrygin, ed., *Algorithms and Programs of Random Search* (Znanie, Riga, 1969), 372 pp.
30. M.Yu. Kataev, V.V. Lazarev, O.Yu. Nikiforova, and I.V. Ptashnik, Atmos. Oceanic Opt. **7**, No. 9, 703–705 (1994).