Journal of Molecular Spectroscopy 316 (2015) 114–118

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Note

The influence of experimental uncertainties in the measured gas pressures and wavenumber scale calibration on multispectrum fitting results

A.E. Protasevich

V.E. Zuev Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Sciences, Academician Zuev Square 1, 634021 Tomsk, Russian Federation

ARTICLE INFO

Article history:
Received 6 July 2015
In revised form 27 July 2015
Available online 28 August 2015

Keywords:
Speed-dependent Voigt
Carbon dioxide
Multispectrum fit

ABSTRACT

The paper considers the artificial corrections of measured gas pressures and wavenumber scale shifts for multispectrum fit by the example of R(22) carbon dioxide self-broadened line of 30013 ← 00001 vibrational band. For this purpose the two quadratic and hypergeometric speed-dependent Voigt line profile models including line mixing within the (Rosenkranz) first-order approximation for line-coupling effects with linear dependences of corresponding model parameters on pressure were applied. The intercomparison of the retrieved results only for pressure corrections, only for wavenumber scale shifts, for both together, and for no correction case demonstrates considerable disagreement between them. The most significant differences in parameters, retrieved in such a way, belong to the first-order line-mixing coefficients and are caused mostly by the shift scattering of wavenumber scale at different pressures.

1. Introduction

In our previous work (the first set of results are published in Ref. [1]) we have tested the ability of quadratic speed-dependent Voigt profile including line mixing [2] (refer in this paper as qSDVPlm) and its hypergeometric predecessor [3,4] (refer in this paper as hSDVPlm) to simulate the six R(12), R(14), R(16), R(18), R(20), R(22) experimentally registered strong quasi-isolated self-broadened lines of carbon dioxide 30013 ← 00001 vibrational band. The details of the experiment and selected results of the data processing can be found elsewhere (see Ref. [1] and references therein). These high-quality, high signal to noise ratio, room-temperature laboratory spectra recorded over a wide pressure range using a high-resolution diode laser spectrometer were transformed to absorption cross-sections and were fitted both spectrum-by-spectrum and using a multispectrum fit procedure to establish whether the model parameters are linear on gas pressure, as it is usually assumed, and to quantify the deviations from linearity. The spectrum-by-spectrum processing leads to much less residuals, than the multispectrum fit, but the behavior of the retrieved parameters is not linear on pressure for some of them. In the multispectrum fit stage we were forced to resort to small changes in "roughly" measured gas pressures to obtain consistency between the line intensities from different spectra, which result in the significant decrease (about two times) of residuals.

Here it should point out Ref. [5], which represents the first direct measurement of weak line mixing coefficients for the 30012 ← 00001 and 30013 ← 00001 vibrational bands of pure carbon dioxide and also accurate values for intensities, self-broadening, self-shift coefficients measured using high-quality Fourier transform spectra. The obtained parameters are in very good agreement with the data of other studies and with the theoretically calculated values. The room temperature spectra were analyzed using the Voigt and the speed-dependent Voigt models, therefore we used the data from Ref. [5] concerning the R(22) line to compare with our values of obtained parameters.

The aim of this paper is to demonstrate the influence of experimental uncertainties in the measured gas pressures and wavenumber scale calibration on multispectrum fitting results using the example of a given CO_2 absorption line. This work has no other purposes (such as a testing of line shape models or a comparison of line profiles).

2. The multispectrum fit using pressure corrections and wavenumber scale shifts

Since the magnitude of relative errors in gas pressure measurements increases at low pressures and decreases at high pressures and the transformation of experimental spectra to the absorption cross-sections requires the division of absorption coefficient by corresponding active gas pressure so the resulting data involve uncertainties in line intensities, which are larger, the lower the

---

E-mail address: A.E.Protasevich@mail.ru

http://dx.doi.org/10.1016/j.jms.2015.08.006
0022-2852/© 2015 Elsevier Inc. All rights reserved.

gas pressure is. To solve this problem one can introduce the “pressure correction factors”, which were adjusted at multispectrum fit. Because of correlation of these new parameters and line intensities at least one pressure correction factor should be set to unity, which means that in this case no pressure correction is used. This implementation should be carried out mostly for the highest pressure (or several pressures), since the prepared data have the smallest relative errors in such a case. Hence in comparison with usual multispectrum fit we will have the number of new adjustable parameters equal to the number of spectra decreased by one at least (it is possible to fix any of these pressure correction factors).

Since the experimental data have errors in the wavenumber scales of spectra it is convenient to introduce the other additive adjustable parameters named here as “wavenumber scale shifts”, which will correct the wavenumber scale. The number of such parameters should be equal to the number of spectra minus two at least (it is possible to fix and any other of these wavenumber scale shifts) because two parameters should be set to zero (that means no wavenumber scale shifts) for spectra preferably at highest and lowest pressures in order to “fix” line center position and shift. Otherwise we get strong correlation between these parameters and line shifts and line center positions resulting in no or bad fit convergence with poor, random parameter set.

For the qSDVPlm our multispectrum fit procedure using the nonlinear least-square fit minimizes the following quantity:

$$\sum_{k=1}^{K}\sum_{j=1}^{J_k}\Big[\sigma_{jk}^{\mathrm{obs}} - \alpha_k S I(\omega_{jk}+\Delta\omega_k;\omega_0,\gamma_0\alpha_kP_k,\gamma_2\alpha_kP_k,\delta_0\alpha_kP_k,\delta_2\alpha_kP_k,$$
$$Y_0\alpha_kP_k) - F_k(\omega_{jk}+\Delta\omega_k)\Big]^2, \qquad (1)$$

where k is the spectrum number, K is the total number of self-broadened CO_2 spectra considered in multispectrum fitting, j is the increment for points in the spectrum, J_k is the number of points in the k-th spectrum, ω_{jk} is the wavenumber corresponding to the j-th point in k-th spectrum, ω_0 is the line center frequency at zero pressure, $\Delta\omega_k$ is the “wavenumber scale shift” for the k-th spectrum, S is the line intensity, γ_0 is the pressure self-broadening coefficient, δ_0 is the self-induced pressure shift coefficient, γ_2 and δ_2 are the line width and the line shift related coefficients in the quadratic speed dependence approximation respectively, Y_0 is the first order line mixing coefficient (everywhere in this paper it is used the so-called Rosenkranz first-order approximation [6] and it is neglected of the speed-dependence of the line-mixing [2]), P_k is the gas pressure of the k-th spectrum, α_k is the “pressure correction factor” for k-th spectrum, $\sigma_{jk}^{\mathrm{obs}}$ is the absorption cross-section (without the wings of neighboring lines, which were excluded on basis of our previous work partially presented in Ref. [1]) derived from k-th experimental CO_2 spectrum at j-th point (corresponding to ω_{jk} wavenumber), $F_k(\omega_{jk})$ is baseline for k-th spectrum calculated at ω_{jk} wavenumber value (in our case all baselines were modeled by polynomials of first order). Furthermore the normalized qSDVPlm line shape from Eq. (1) is given by [2]

$$I(\omega;\omega_0,\Gamma_0,\Gamma_2,\Delta_0,\Delta_2,Y) = \frac{c}{\sqrt{\pi}\omega_0\tilde{v}}\mathrm{Re}\{(1+iY)[w(iZ_1)-w(iZ_2)]\}, \qquad (2)$$

$$Z_1 = \sqrt{\frac{(\Gamma_0-3\Gamma_2/2)+i(\omega-\omega_0-\Delta_0+3\Delta_2/2)}{\Gamma_2-i\Delta_2}+\left(\frac{\omega_0\tilde{v}}{2c(\Gamma_2-i\Delta_2)}\right)^2} - \frac{\omega_0\tilde{v}}{2c(\Gamma_2-i\Delta_2)}, \qquad (3)$$

$$Z_2 = \sqrt{\frac{(\Gamma_0-3\Gamma_2/2)+i(\omega-\omega_0-\Delta_0+3\Delta_2/2)}{\Gamma_2-i\Delta_2}+\left(\frac{\omega_0\tilde{v}}{2c(\Gamma_2-i\Delta_2)}\right)^2} + \frac{\omega_0\tilde{v}}{2c(\Gamma_2-i\Delta_2)}, \qquad (4)$$

where ω is the current frequency, c is the speed of light, ω_0 is the unperturbed frequency, $w(z) = \exp(-z^2)\mathrm{erfc}(-iz)$ is the complex probability function, Y is the first-order line-mixing parameter [2,6], assumed speed independent, $\tilde{v} = \sqrt{2k_BT/m_a}$ is the most probable speed for an absorbing molecule of mass m_a, k_B is the Boltzmann constant, T is the gas temperature, and finally Γ_0, Γ_2, Δ_0 and Δ_2 are the quadratic speed dependence parameters [2], assuming a quadratic speed-dependence of collisional width $\Gamma(v)$ and shift $\Delta(v)$ on the speed of absorbing molecule v, i.e. $\Gamma(v) - \mathrm{i}\Delta(v) = (\Gamma_0 - i\Delta_0) + (\Gamma_2 - i\Delta_2)\lfloor(v/\tilde{v})^2 - 3/2\rfloor$.

Similarly, one can write down the expressions needed to perform a non-linear least squares fit based on hSDVPlm. In this case our multispectrum fit procedure using the nonlinear least-square fit minimizes the following quantity:

$$\sum_{k=1}^{K}\sum_{j=1}^{J_k}\Big[\sigma_{jk}^{\mathrm{obs}} - \alpha_k S\tilde{I}(\omega_{jk}+\Delta\omega_k;\omega_0,\gamma_0\alpha_kP_k,\delta_0\alpha_kP_k,Y_0\alpha_kP_k,m,n)$$
$$-F_k(\omega_{jk}+\Delta\omega_k)\Big]^2, \qquad (5)$$

where m and n are the exponents of power laws $\Gamma(v_r) \propto v_r^m$ and $\Delta(v_r) \propto v_r^n$ of speed dependence of collisional width and shift on

Table 1
Experimental setup and gas conditions.

Configuration and conditions	Two-channel diode laser spectrometer and vacuum system for preparation of gas mixtures
Light source	DFB laser (NEL, $\lambda \approx 1.6$ μm)
Range of tuning	Δv = 1.0–1.2 cm^{-1}
Accuracy of the laser crystal temperature	2×10^{-4} °C
Laser power	≈15 mW
Laser line half-width	⩾6 MHz
Resolution	0.0001 cm^{-1}
Signal-to-noise	~7000
Photodetectors	InGaAs [http://jp.hamamatsu.com]
Diameter of the analytical cell	30 mm
Length of the analytical cell	199.80 ± 2 cm
Pressure sensors	“Elemer” AIR-20/M2 (measurement range 0–100 kPa with an error of 0.2%) and “Sensor” (measurement range 0–10 kPa with an error of 0.1%)
Gas sample temperature	296 K
Calibration standards used	CO_2
CO_2 pressure range	16–586 Torr
Isotope composition of pure CO_2 sample	Natural abundance