Spectral line-shapes of oxygen B-band transitions measured with cavity ring-down spectroscopy

S Wójtewicz, A Cygan, P Masłowski, J Domysławska, P Wcisło, M Zaborowski, D Lisak*, R S Trawiński and R Ciuryło

Institute of Physics, Faculty of Physics, Astronomy, and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Toruń, Poland
E-mail: dlisak@fizyka.umk.pl

Abstract. Results of line-shape measurements of self- and N₂-broadened P9 P9 transition of the oxygen B band are presented. Spectra were acquired using the optical frequency comb-assisted Pound-Drever-Hall-locked frequency-stabilized cavity ring-down spectrometer (PDH-locked FS-CRDS). In the line-shape analysis the line narrowing described by Dicke narrowing or/and the speed dependence of collisional broadening were taken into account. The multi-spectrum fitting technique was used to minimize numerical correlations between line-shape parameters. Collisional broadening and shifting coefficients are reported with sub-percent uncertainties. Influence of the spectral line-shape model used in data analysis on determined line intensities and collisional broadening is discussed.

1. Introduction

Systematic progress in experimental techniques of molecular spectroscopy and spectral line shape investigation is stimulated by increasing demands in high precision remote sensing of atmosphere composition, metrological applications and testing fundamental physics. Spectroscopic molecular databases, e.g. [1,2], containing line-by-line parameters, are in most cases based on the Voigt profile (VP). This simplification generally does not allow to reproduce experimental data with sub-percent accuracy. It is well established that such physical effects as velocity-changing collisions, which lead to Dicke narrowing of line, and dependence of the collisional broadening and shifting on molecules speed, called speed-dependent effects, must be taken into account [3,4] to model the line shape with sub-percent accuracy. As recently proposed [5,6] and recommended in Ref. [7] the new generation spectroscopic databases may easily incorporate these two effects and additionally effect of correlation between VC and phase/state-changing collisions [8] by using the partially correlated speed-dependent Nelkin-Ghatak profile PCSDNGP [9] with quadratic speed dependence [10] instead of the Voigt profile. This profile, also called Hartmann-Tran profile (HTP), can be calculated almost as fast as Voigt profile [5,11]. On the other hand it is known that simple models of quadratic speed-dependence, as well as the hard-collision approximation of velocity-changing collisions used in PCSDNGP are not optimal for description of many molecular systems.

In this paper we report progress in systematic study of spectral line shapes of O₂ transitions from the B-band \( b^1Σ^+ (v = 1) \leftarrow X^3Σ^− (v = 0) \). In our earlier papers [12–16] self-broadened lines were studied. High signal-to-noise ratio experimental spectra enabled us to study advanced...
line-shape effects, such as velocity-changing collisions, speed-dependent effects, and correlations between velocity- and phase-changing collisions. This analysis is now extended to the case of perturbation by a mixture \( \text{N}_2 – \text{O}_2 \), in which both self and foreign broadening has to be considered. This is nontrivial for the speed-dependent profiles, however when quadratic model of speed dependence is used a gas mixture can be treated as single perturber with effective speed dependence parameters [17].

2. Experimental setup

Experimental line shapes of \( \text{O}_2 \) were measured with PDH-locked FS-CRDS described in Refs. [16, 18]. The length of the high-finesse ring-down cavity is stabilized to the HeNe laser with frequency stability of 1.5 MHz. The probe laser (ECDL) is locked to the consecutive TEM\(_{00}\) modes of the cavity with the PDH method [19]. This enables to maximize power and repetition rate of the ring-down signals [20, 21] and obtain typical SNR of spectra as high as \( 10^4 \), or even \( 2 \times 10^5 \) with long-term averaging [14]. The absolute frequency of the probe laser is measured at each point of the spectrum by the optical frequency comb [13]. This scheme leads to a combined standard uncertainty of the spectrum frequency axis lower than 200 kHz.

To prepare a sample of \( \text{N}_2 – \text{O}_2 \) gas mixture individual gases with purity of 99.999% were mixed in a vacuum chamber equipped with a fan to assure uniform mixing. For the investigated P9 P9 transition the optimal gas composition was 3% of \( \text{O}_2 \) in \( \text{N}_2 \). The pressures were measured with Baratron gauges having relative uncertainties of 0.05% and temperature of the ring-down cavity was stable to 0.1 K during a single spectrum measurement.

3. Results and discussion

Systematic study of subtle line-shape effects requires to use a multi-spectrum fitting technique to avoid problem of numerical correlations between fitted parameters [22]. Also for this reason spectra were measured in a wide pressure range (10 - 400) Torr. In Fig. 1 experimental profiles of \( \text{O}_2 \) P9 P9 line broadened by mixture of \( \text{N}_2 – \text{O}_2 \), are shown with residuals from fits of Voigt profile (VP), speed-dependent Voigt (SDVP) and the speed-dependent Nelkin-Ghatak profile (SDNGP).In the latter two models the quadratic speed dependence was used. For each residuals the quality of the fit (QF) factor, defined as a peak absorption divided by the standard

![Figure 1. Experimental profiles of \( \text{O}_2 \) P9 P9 line broadened by \( \text{N}_2 – \text{O}_2 \) mixture, and residuals from multi-spectrum fits of VP, SDVP and SDNGP.](image-url)
deviation from residuals [14], was calculated. As seen in Fig. 1 incorporation of the speed-
dependent effects to the model improves the QF by an order of magnitude. Taking both the
speed dependence and velocity-changing collisions into account in the SDNGP further improves
the QF, but only by 7% comparing to the SDVP.

In Fig. 2 relative differences of line intensity $S$ and collisional width $\gamma_L$ obtained from
multi-spectrum fits of different models to $N_2$-broadened P9 P9 oxygen line are presented. The
reference profile corresponding to zero in both plots is the SDNGP. Here additionally to the
previously described models we considered also the Galatry (GP), Nelkin-Ghatak (NGP) and
the speed-dependent Galatry (SDGP) [23, 24] profiles. Clearly all the speed-dependent profiles
give consistent $S$ and $\gamma_L$ to within 0.2%, while the profiles that consider velocity-changing
collisions, but not speed-dependent effects differ by up to 1%, depending on velocity-changing
model. The Voigt profile leads to systematic errors of 1.5% for $S$ and 5% for $\gamma_L$.

Comparison of the line-shape parameters for self- and $N_2$-broadened P9 P9 oxygen line
obtained from the SDVP fits is given in Table 1. Parameters for $N_2$ broadening were calculated
from results for $N_2$ – $O_2$ mixture with use of self-broadening results. Because of low gas pressures
used for self-broadening experiment the $a_S$ could not be determined. Comparing $a_W$ parameters
it seems that the speed-dependent effects are significantly stronger in case of perturbation by
$N_2$ than $O_2$.

**Table 1.** Line-shape parameters for self- and $N_2$-broadened P9 P9 oxygen line with
their standard deviations, obtained from the SDVP fits. $\gamma_L/N$ and $\delta/N$ in units
($10^{-19}$GHz/(molec./cm$^3$)). Line intensity $S$ in units ($10^{-25}$cm$^{-1}$/(molec. cm$^{-2}$)).

| perturber | $S$ at $T=296$ K | $\gamma_L/N$ | $\delta/N$ | $a_W$ | $a_S$ |
|-----------|-----------------|-------------|-----------|-------|-------|
| $O_2$     | 5.411(27)       | 1.118(5)    | -0.0956(14) | 0.0497(10) | -     |
| $N_2$     | –               | 1.231(9)    | -0.1183(9) | 0.0935(10) | -0.0267(5) |
4. Conclusions
We presented systematic line-shape study of the oxygen B-band transition P9 P9. It revealed that satisfactory quality of the fits of the model profiles to the experimental data for line perturbed by N\textsubscript{2} can be achieved with the speed-dependent Voigt profile. The influence of Dicke narrowing is not evident, as the speed-dependent Nelkin-Ghatak profile leads to nearly equal quality of the fit as SDVP. This can be explained in terms of correlations between velocity- and phase-changing collisions, which effectively reduce Dicke narrowing.

High-precision line-shape parameters of the investigated speed-dependent Voigt profile, given in the paper allows one to reproduce experimental spectra with relative precision better than 1:4000, which is ten times better than the commonly used Voigt profile.

Acknowledgments
The research is part of the program of the National Laboratory FAMO in Toruń, Poland, and is supported by the Polish National Science Centre Project nos. DEC-2011/01/B/ST2/00491 and UMO-2012/05/N/ST2/02717. The research is also supported by the Foundation for Polish Science TEAM and HOMING PLUS Projects co-financed by the EU European Regional Development Fund. A. Cygan is supported by the Foundation for Polish Science START Project.

References
[1] Rothman L S et al. 2013 J. Quant. Spectrosc. Radiat. Transf. 130 4
[2] Jacquinet-Husson N et al. 2011 J. Quant. Spectrosc. Radiat. Transf. 112 2395
[3] Duggan P, et al. 1997 J. Mol. Spectrosc. 186 90
[4] Ciuryło R, Pine A S, Szudy J 2001 J. Quant. Spectrosc. Radiat. Transf. 68 257
[5] Ngo N H, Lisak D, Tran H, Hartmann J-M 2013 J. Quant. Spectrosc. Radiat. Transf. 129 89
[6] Ngo N H, Lisak D, Tran H, Hartmann J-M 2014 J. Quant. Spectrosc. Radiat. Transf. 134 105
[7] Tennyson J, et al. 2014 Pure. Appl. Chem. in press.
[8] Rautian S G and Sobelman I I 1967 Sov. Phys. Usp. 9 701
[9] Pine A S 1999 J. Quant. Spectrosc. Radiat. Transf. 62 397
[10] Rohart F, Mader H, Nicolaisen H-W 1994 J. Chem. Phys. 101 6475
[11] Tran H, Ngo N H, Hartmann J-M 2013 J. Quant. Spectrosc. Radiat. Transf. 129 199
[12] Wójtewicz S, Lisak D, Cygan A, Domysławská J, Trawiński R S and Ciuryło R 2011 Phys. Rev. A 84 032511
[13] Domysławská J, et al. 2012 J. Chem. Phys. 136 024201
[14] Cygan A, et al. 2012 Phys. Rev. A 85 022508
[15] Domysławská J, et al. 2013 J. Chem. Phys. 139 194312
[16] Wójtewicz et al. 2014 J. Quant. Spectrosc. Radiat. Transf. 144 36
[17] Lisak D, Cygan A, Wcisło P and Ciuryło R 2015 J. Quant. Spectrosc. Radiat. Transf. 151 43
[18] Cygan A, et al. 2013 Eur. Phys. J.-Spec. Top. 222 2119
[19] Drever R W P, et al. 1983 Appl. Phys. B 31 97
[20] Cygan A, et al. 2011 Rev. Sci. Instrum. 82 063107
[21] Cygan A, et al. 2011 Meas. Sci. Technol. 22 115303
[22] Benner C, et al. 1995 J. Quant. Spectrosc. Radiat. Transf. 53 705
[23] Ciuryło R and Szudy J 1997 J. Quant. Spectrosc. Radiat. Transf. 57 411
[24] Priem D, et al. 2000 J. Molec. Struct. 517 435