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

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Abstract. Results of line-shape measurements of self- and N_2-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 O_2 transitions from the B-band ($b\,^1\Sigma_g^+(v=1) \leftarrow X\,^3\Sigma_g^-(v=0)$). 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 $N_2 - O_2$, 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 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 2×10^5 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 $N_2 - O_2$ 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 O_2 in 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
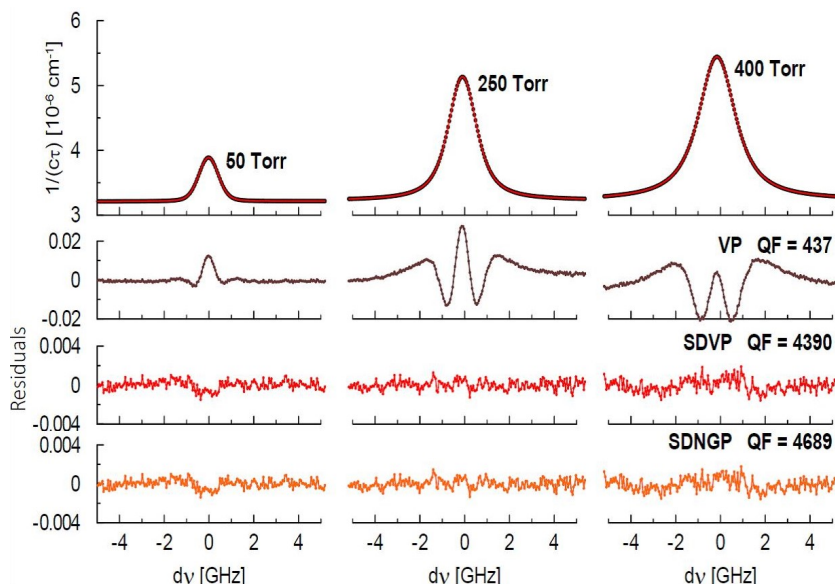

Figure 1. Experimental profiles of O_2 P9 P9 line broadened by N_2 – O_2 mixture, and residuals from multi-spectrum fits of VP, SDVP and SD-NGP.

of O_2 P9 P9 line broadened by mixture of $N_2 - O_2$, 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

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 γ_L obtained from multi-spectrum fits of different models to N_2-broadened P9 P9 oxygen line are presented. The
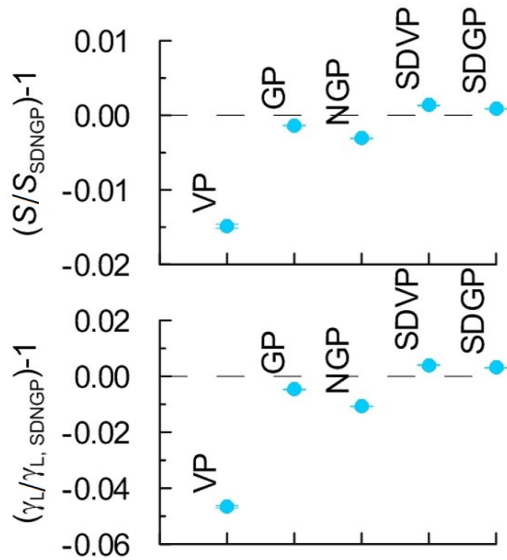

Figure 2. Relative differences of line intensities S and collisional widths γ_L obtained from multi-spectrum fits of different models to N_2-broadened P9 P9 oxygen line. The reference profile is SDNGP.

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 γ_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 γ_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. γ_L/N and δ/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	γ_L/N	δ/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_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.

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