Dispersion and relativistic corrections to the spectral line-shape models

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Abstract. We investigate the influence of dispersion and relativistic effects on the spectral line-shape models on an example of simple Gaussian and Voigt profiles. We show that dispersion and relativistic corrections can affect the line shape even at the relative level of $10^{-5}$.

1. Introduction
Recent developments in ultra-high signal-to-noise-ratio spectroscopic measurements show that the commonly used theoretical line-shape profiles should be supplemented by the do far neglected very subtle physical effects. Here we focus on the dispersion and relativistic deformations of the line-shape models. We report the dispersionally corrected Gaussian profile describing Doppler broadening and resulting from the frequency dependence of the Doppler shifting caused by dispersion [1, 2] as well as the light frequency variation over the whole spectral line shape [2]. We also derive the relativistic Voigt profile taking into account both the homogeneous and Doppler broadening in the case of spontaneous emission [3] and we discuss several properties of both profiles. These effects can affect the spectral line shapes even at the level of $10^{-5}$ and influence the determination of the line position at kHz level. The presented results are crucial in Doppler-width thermometry [1, 4], the determination of the interaction potentials [5], precise molecular spectroscopy for fundamental studies [6], and the development of astrophysical models.

2. Dispersionally corrected Gaussian profile
The thermal motion of the absorbing or emitting molecules leads to the Doppler broadening of the spectral line shape described by the Gaussian profile (GP). In derivation of the GP the module of the wave vector $\vec{k}$ is assumed to be constant and equal to $k_0 = \omega_0/c$ where $\omega_0$ is the unperturbed line frequency and $c$ is the speed of light in vacuum. This assumption results in the full Doppler width at half maximum equal to $\gamma_D = 2\sqrt{\ln 2} \omega_D$, where $\omega_D = k_0 v_m$, $v_m = \sqrt{2k_BT/m}$ is the most probable absorber speed, $m$ is the absorber mass, $T$ is the gas temperature, and $k_B$ is the Boltzmann constant. However, the value of $k$ within the line profile is not constant but depends on the frequency $\omega$. In order to properly describe this frequency...
dependence two effects have to be taken into account: the unperturbed line frequency \( \omega_0 \) should be replaced by the light frequency \( \omega \) and the speed of light in vacuum \( c \) should be replaced by the speed of light in the sample \( c/n_\alpha(\omega) \) leading to the relation \( k(\omega) = \omega n_\alpha(\omega)/c \). The complex refractive index \( n_\alpha(\omega) \) consists of both nonresonant and resonant components. The latter are related to the complex line-shape function which means that the calculation of the dispersionally corrected GP requires an iteration procedure.

The simulations were made for the very strong \(^{12}\text{C}^{16}\text{O}_2\) R16e transition from the \(^{12}\text{C}^{16}\text{O}_2\) (00011) \( \leftarrow \) (00001) band at the temperature \( T = 296 \text{ K} \) and pressure \( p = 4 \text{ Pa} \). Its wavenumber and line intensity are \( \bar{\nu}_0 = 2361.46591 \text{ cm}^{-1} \) and \( S = 3.543 \times 10^{-18} \text{ cm}^{-1}/(\text{molecule/cm}^2) \), respectively [7]. The simulations showed that the change in Doppler width is mainly caused by the nonresonant part of the refractive index while its resonant component, together with the light frequency variation over the whole profile, cause line shift. The differences between the dispersionally corrected GP and the ordinary GP for the investigated \( \text{CO}_2 \) line are presented in Fig. 1. It can be seen that in this case the dispersion corrections affect the line shape at a level of \( 10^{-5} \) and shifts the line position by about \( -1.1 \text{ kHz (}-1.4 \times 10^{-5} \omega_D\text{)} \) while the relative change of the value of the Doppler width is only \( 4 \times 10^{-8} \).

![Figure 1](image1.png)

**Figure 1.** Top panel: the Gaussian profile. Bottom panel: differences between dispersionally corrected GP and ordinary GP for the investigated \( \text{CO}_2 \) transition.

![Figure 2](image2.png)

**Figure 2.** Top panel: the Voigt profile. Bottom panel: differences between relativistic VP and ordinary VP for \( \beta_m = 10^{-4} \) and \( \Gamma/\omega_D = 1 \).

### 3. Relativistic Voigt profile

The inclusion of the relativistic effects to the spectral line-shape models was limited to the emissive [8] as well as absorptive [9] Gaussian profile describing the relativistic Doppler effect. Here we investigate the more sophisticated case of the emissive relativistic Voigt profile (VP).

A detailed derivation of the relativistic VP and the assumptions made during it as well as the final expression for the profile can be found in Ref. [3]. Here we briefly describe several properties of this profile. The relativistic VP is described by three parameters: \( \omega_D \), \( \Gamma \) (the half collisional width at half maximum) which characterize also the classical Voigt profile, and \( \beta_m = v_m/c \) which controls the magnitude of the relativistic effects. It can be shown that this formulation of the relativistic VP has proper asymptotic behavior in the cases of the classical VP (corresponding to \( \beta_m \rightarrow 0 \)) and the relativistic GP (corresponding to \( \Gamma/\omega_D \rightarrow 0 \)) [8]. It can be proved analytically that this profile is normalized. An alternative expression, which simplifies the numerical evaluation for the most physically meaningful weak-relativistic regime, was also derived.
Molecular hydrogen is the most obvious target for searching of the relativistic line-shape deformations due to its small mass. The differences between the relativistic VP and the classical VP for $\beta_m = 10^{-4}$ and $\Gamma/\omega_D = 1$ are presented in Fig. 2. It should be noted that $\beta_m$ value of $10^{-4}$ is close to the dissociation limit for the molecular hydrogen and corresponds to the conditions that can be met in hot stars. On the other hand the estimated relativistic correction at room temperature is at the level of $10^{-6}$.

4. Conclusions
We showed that the dispersion and relativistic corrections to the spectral line shapes are not negligible and could be observed using present spectrometers [10, 11]. These effects can affect the line shapes at the level of $10^{-5}$. The resulting profiles are mainly asymmetric and can influence the line position determination at the level of a few kHz which is comparable to the accuracy of the best Doppler-limited measurements of the line position [12].

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