Analysis of Wavelength Modulation Spectra for Determination of OH Radical Concentration in an Atmospheric Pressure Laminar Premixed Flames

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Abstract. This work is aimed at the application of wavelength modulation spectroscopy with the second harmonic detection for determination of OH radical concentration in laminar premixed flames of methane-air mixtures. Several hot water lines and two overtone OH transitions were identified in high-resolution absorption spectra measured in our experimental setup. Information on spectral line-shape parameters for selected OH transitions were extracted from the experimental data using relevant methods and approximations. An appropriate line-shape model was finally implemented into an automated least-square fitting procedure in order to quantify the local mole fraction of OH radical in an atmospheric pressure flames.

1. Introduction
The quantification of hydroxyl (OH) radical concentration in the harsh environment of flames is of significant importance for practical combustion diagnostics as well as for validation of chemical kinetic models. Previous investigators dealing with application of wavelength modulation spectroscopy with the second harmonic detection (i.e. 2f−WMS technique) for the given task reported an interference of the OH transitions with hot-water lines in the near infrared region as a major source of measurement errors and discrepancies [1]. Therefore, it is desirable to develop and implement an adequate approach for extracting spectral absorption features of OH radical from 2f−WMS experiments performed in laboratory flames.

2. Methodology
An analysis presented here is focused on the narrow spectral region (within 6360±1 cm−1) which we investigated recently in our laboratory. A pair of OH absorption lines amenable in the given range (see e.g. [2]) was probed in a laminar premixed flame employing the 2f−WMS technique. Spectral line shape parameters of selected transitions were derived from the difference spectrum measured at two distinct vertical positions in stoichiometric methane-air flat flame.
2.1. Experimental setup
Measurements were performed under atmospheric pressure using a laminar premixed flat flame burner designed according to Hartung et al. [3]. The water cooled body of the burner was mounted on a manually driven vertical translation stage to enable its movement relative to optical path thus to adjust appropriate height above burner (HAB). Two separate mass-flow controllers were employed to prepare the methane-air mixture at the desired equivalence ratio ($\Phi = 1.0$) and volumetric flow rate ($Q_v = 10 \text{ ln/min}$). More detailed information on the experimental apparatus employed for 2f–WMS measurements and the post-processing methodology is provided elsewhere [4].

2.2. Spectral line shape models
A second derivative of the Lorentzian function $L$ (referred to as the Model 1) provides a zeroth-order approximation of the 2f–WMS signal ($S_{2f}$) when pressure broadening has a dominating effect on spectral line shape and width $\Delta \nu$, i.e. its half-width at half maximum (HWHM). Alternatively, a second derivative of the so-called Pearson type VII distribution function $P_{VII}$ (referred to as the Model 2) can be utilized as an approximation of $S_{2f}$ if the Voigt profile is the more appropriate spectral line shape model, i.e. if the effect of Doppler broadening is also taken into account.

Fourier series expansion has previously been employed [6] to derive an analytical expressions of line-shape functions relevant to 2f–WMS signals broadened by frequency modulation (FM). As the most simplistic model from this class, the so called Arndt formula [7] was applied (referred to as the Model 3). The modulation amplitude $\nu_a$ was evaluated from the least-squares fit of the experimental spectrum assuming Lorentzian profile of the given absorption line, i.e. $\Delta \nu \approx \delta \nu_L$.

Consequently, the De Tommasi approximation [8] (referred to as the Model 4) was used to estimate $S_{2f}$ when assuming the Voigt line profile. The spectral line shape was evaluated as a linear combination of the Doppler-broadened profile (with $\delta \nu_G$, i.e. HWHM of the Gaussian function) and pressure-broadened profile (with $\delta \nu_L$, i.e. HWHM of the Lorentzian function). The idealized case of pure FM was presumed considering moderate modulation frequency ($f = 11 \text{ kHz}$) and relatively low modulation amplitudes $\nu_a$ for the experiment reported here.

3. Results and discussion
Spectral line-shape models presented above were utilized to estimate particular parameters of interest for the selected OH absorption line (at 6360.75 cm$^{-1}$), which is the $f$–parity component of the rovibrational transition within the $X^2\Pi_{1/2}$ state. The particular transition between lower ($J'' = 11.5f$) and upper ($J' = 10.5f$) $\Lambda$-split rotational quantum levels of the OH radical belongs to its vibrational overtone ($v'' = 0 \rightarrow v' = 2$) band.

An excerpt of the difference spectrum $\Delta S_{2f}$ (obtained by subtraction of the $S_{2f}$ signals measured in flame at HAB = 10 mm and HAB = 3 mm respectively) is depicted in the Figure 1. The identical spectrum is shown in the Figure 2 with a modified intensity scale after normalization to OH peak height (yielding $\tilde{\Delta} S_{2f}$). It is worth noting that the given OH line was omitted from previous analysis [2] due to the presence of interfering water absorption features. However, characteristic $S_{2f}$ profiles of two H$_2$O absorption lines remained well-resolved in the residual spectrum, especially in the Figure 2. The most appropriate fitting performance can be concluded for the Model 4 in this case with deviations mostly below $\pm3\%$ when considering the slight offset of the experimental data.

4. Concluding remarks
Based on the results of this work it can be concluded that the Doppler broadening and pressure-broadening effects need to be considered simultaneously for estimating accurate 2f–WMS line profile of OH radical in high-temperature combustion environment.
Figure 1. Experimental spectrum ($\Delta S_{2f}$) depicted within the wavenumber scale showing the experimental profile of the OH (P11.5f) transition and neighboring H$_2$O lines in the upper trace and residuals of the Model 1 (Solid) and the Model 2 (Dotted) in the lower trace.

Relevant analytical models (based on Voigt profile) can be further improved by assuming line-shape asymmetry of 2f–WMS signals [4]. The approximation of De Tommasi et al. [8] was implemented via an automated least-squares fitting procedure for quantifying local mole fraction of OH radical in atmospheric-pressure flame based on 2f–WMS measurement.

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References
[1] Aizawa T 2001 Applied Optics 40 4894 ISSN 0003-6935, 1539-4522
[2] Rutkowski L, Johansson A C, Valiev D, Khodabakhsh A, Tkacz A, Schmidt F M and Foltynowicz A 2016 Photonics Letters of Poland 8 110 ISSN 2080-2242
[3] Hartung G, Hult J and Kaminski C F 2006 Measurement Science and Technology 17 2485–2493 ISSN 0957-0233, 1361-6501
[4] Nevrý V, Klec̆ka V, Vašinek M, Válek V, Suchanek J, Dostál M, Hric B, Bitala P and Zelinger Z 2018 Measurement Science Review 17 157–160
[5] Pearson K 1916 Phil. Trans. R. Soc. Lond. A 216 429–457 ISSN 0264-3952, 2053-9258
[6] Kluczynski P, Gustafsson J, Lindberg A M and Axner O 2001 Spectrochimica Acta Part B: Atomic Spectroscopy 56 1277–1354 ISSN 0584-8547
[7] Arndt R 1965 Journal of Applied Physics 36 2522–2524 ISSN 0021-8979, 1089-7550
[8] De Tommasi E, Castrillo A, Casa G and Gianfrani L 2008 Journal of Quantitative Spectroscopy and Radiative Transfer 109 168–175 ISSN 00224073