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TDLAS-based photofragmentation spectroscopy for detection of K and KOH in flames under optically thick conditions

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Photofragmentation spectroscopy is combined with tunable diode laser absorption spectroscopy to measure the line shape of the fragment species. This provides flexibility in choosing the UV pulse location within the line shape and accurate quantification of both target species and background fragment concentrations, even under optically thick conditions. The technique is demonstrated by detection of potassium hydroxide (KOH) and atomic potassium K(g) above solid KOH converted in a premixed methane-air flat flame. Time series of KOH(g) and K(g) concentrations are recorded as a function of solid KOH mass and flame stoichiometry. The total substance released during the conversion is in good agreement with the initial solid KOH mass. Under fuel-rich conditions, increased K(g) concentrations at the expense of KOH(g) are observed compared to thermodynamic equilibrium. © 2020 Optical Society of America

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The increasing interest in renewable, CO₂-neutral energy sources has propelled the importance of biomass combustion and gasification in the energy industry. Most types of biomass contain a large amount of potassium (K), which is released to the gas phase mainly as atomic potassium K(g), potassium chloride (KCl), and potassium hydroxide (KOH) [1]. KOH(g) is one of the most abundant and reactive trace species in biomass boilers and heavily involved in ash-formation, slagging, fouling, and corrosion [2,3]. Optical *in situ* diagnostics of K species is an important tool to improve the understanding of the underlying chemistry and enable reliable process monitoring [4].

Existing spectroscopic techniques to selectively detect KOH(g) *in situ* include direct UV absorption [5–7], laser induced fluorescence [8], and collinear photofragmentation (PF) atomic absorption spectroscopy (CPFAAS) [9,10]. The latter method was developed by Sorvajärvi *et al.* and bears similarities to other implementations of photofragmentation absorption spectroscopy [11,12]. CPFAAS has emerged as the most sensitive method for quantitative assessment of K species in high temperature environments and was

successfully employed in laboratory reactors [13–15] and full-scale combustion boilers [16].

In CPFAAS, a pulsed UV laser is used to dissociate the target molecules into fragments that are probed using laser absorption spectroscopy. The initial fragment absorption (PF signal) induced by the UV pulse is related to the target species concentration and followed by an exponential decay due to the recombination of the fragments [10]. So far, the technique has been used with a fixed probe laser frequency, often actively locked to the absorption line center of the fragment species. However, the PF signal contrast depends on the background concentration of the detected fragment species, which, in the case of K(g), can vary over several orders of magnitude depending on the chemical composition of the fuel, stoichiometry, and gas temperature [17]. This can lead to high absorbance conditions, such that the transmitted probe laser intensity is below the detector threshold around line center, and the PF signal can no longer be resolved [18]. Although the fixed probe laser frequency can be detuned from line center in the CPFAAS approach [16], accurate quantification requires knowledge about the prevailing K(g) absorption line shape (broadening).

Here, we combine photofragmentation spectroscopy with tunable diode laser absorption spectroscopy (PF-TDLAS) by rapidly scanning the probe laser frequency across the absorption profile of the fragment species. This has the advantage that the fragment line shape, and thus accurate concentrations of both KOH(g) and K(g), can be obtained, even under optically thick conditions. In addition, the position of the PF signal within the K(g) line shape can be flexibly chosen, eliminating the need for external locking schemes.

In PF-TDLAS, the PF signal baseline is not constant, but includes a frequency dependent variation given by the fragment absorption profile, which thus is incorporated in the theoretical model. The PF signal intensity (UV pulse at time $t = 0$) is then given by

$$I(t, \nu) = \begin{cases} I_0(\nu) + C & t < 0 \\ I_0(\nu) \exp(-\alpha(t, \nu)) + C & t \geq 0 \end{cases}, \quad (1)$$

where I_0 is the PF signal baseline, α is the absorbance due to the induced fragments, and C is an offset parameter.

Fig. 1. Experimental PF-TDLAS setup. C—collimating optics, M—mirror, DM—dichroic mirror, L—lens, F—filter, EM—energy meter, BS—beam splitter, HBW/LBW-PD—high/low bandwidth photodetector, DAQ—data acquisition system, Amp—pre-amplifier, and Osc—oscilloscope.

The absorbance depends on several parameters, including analyte concentration, absorption path length, UV energy, and absorption cross sections of analyte and fragments [10]. The frequency dependence of I_0 due to the TDLAS scan is obtained from the measurement of the fragment line shape [18].

A schematic drawing of the experimental setup for detection of KOH(g) and K(g) using PF-TDLAS is shown in Fig. 1. Since KOH(g) reacts with common furnace materials like quartz and mullite [3,13,15], the technique is validated using a laboratory burner. The water-cooled (0.5 L/min), atmospheric flat-flame burner [19] is fueled with methane/air mixtures set with the help of mass flow controllers (MKS, GM50A) to yield air-to-fuel equivalence ratios, ϕ , between 0.7 and 1.15. The total flow rate is kept at 10 L/min. A known amount of solid KOH is placed on a platinum plate (diameter 5 mm), which is then positioned 2 mm above the surface of the burner on platinum/rhodium wires that also serve as S-type thermocouple measuring the plate temperature. The KOH(s) sample is prepared such that first a solution with 3.3 μmole KOH per droplet is placed on the plate, then dried on a hot plate and finally weighted using a scale with 10 μg resolution (Mettler Toledo XS205). An uncertainty of 20 μg is assumed for the sample weight.

The PF-TDLAS technique is realized employing a compact, diode pumped Q-switched Nd:YAG laser emitting 1.3 ns pulses at 355 nm (CryLas FTSS 355-300) for KOH(g) fragmentation, and a near-infrared (NIR) distributed-feedback diode laser (Nanoplus) that is scanned over the potassium D1 line at 769.9 nm. The UV pulse energy incident on the sample was $249 \pm 2 \mu\text{J}$, and the repetition rate was set to 40 Hz. The NIR laser had an output power of 2 mW and was scanned over 0.25 nm (4.2 cm^{-1}) at 40 Hz. In order to share the same beam path through the sample volume, the UV and NIR beams are combined using a dichroic mirror (DM, Semrock FF376-Di01). The UV beam diameter was $1.1 \pm 0.1 \text{ mm}$, and the NIR beam diameter was $1.2 \pm 0.1 \text{ mm}$. After passing the sample, the beams are again separated using a second DM. The UV beam is expanded (L1, Thorlabs LD4771-UV), attenuated (F1, Thorlabs NDUV05A), and directed onto an energy meter (EM, Thorlabs ES111C) to measure the transmitted pulse energy. The NIR beam is separated using a 90/10 beam splitter (BS, Thorlabs BSX11), which directs 90% of the laser power to a high-bandwidth detector (HBW-PD, Thorlabs DET10A) to measure the PF signal and 10% to a low-bandwidth detector (LBW-PD, Thorlabs PDA36A-EC) to measure the K(g)

absorption profile. Each detector is equipped with a focusing lens (L2, Thorlabs LA1131-B) and a band-pass filter (F2, Thorlabs FB770-10).

The PF signal is amplified (Amp, Stanford Research Systems SR445A) and recorded with an oscilloscope (Osc, Rohde & Schwarz RTM3004), while the TDLAS signal is digitized with a DAQ-card (National Instruments PXIe-6356). The UV laser trigger and NIR laser scan are controlled and synchronized using a digital function generator (National Instruments PXI-5402), resulting in one UV pulse per NIR laser scan. The signals are averaged 20 times, which provides an overall temporal resolution of 0.5 s.

PF-TDLAS measurements were carried out 15 mm above the platinum plate in the flame. The K(g) concentrations were obtained by fitting the K(g) absorption profiles to the models presented in Refs. [7,18] with K(g) concentration and collisional width as open parameters. The KOH(g) concentrations were determined by fitting the K(g) decay curves following the UV pulse to the model in Ref. [10], but using Eq. (1), with KOH(g) concentration and decay time constant as open parameters. The temperature was a fixed value obtained from water vapor two-line thermometry at 1398 nm [20]. The absorption cross sections for KOH(g) at the flame temperatures were taken from [6]. The difference in UV pulse energy before and after the KOH(g) sample was indistinguishable from the pulse-to-pulse variations and detector noise, therefore, in this work it was sufficient to measure the pulse energy after the sample volume. The absorption path length, i.e. the diameter of the plume, was determined during stable KOH vaporization by moving the burner horizontally until K absorption was negligible. The distribution of K(g) and KOH(g) in the plume resembled a Gaussian shape, from which the path length was estimated to $20 \pm 1 \text{ mm}$. This is in accordance with [21], where pellets of similar size were used as point sources of K(g).

Typical simultaneously measured K(g) absorption profiles and PF signals are displayed in Fig. 2 for a fuel-lean ($\phi = 0.8$) and fuel-rich ($\phi = 1.1$) flame. The gas temperatures 15 mm above the platinum plate were $1790 \pm 25 \text{ K}$ and $2050 \pm 25 \text{ K}$ for $\phi = 0.8$ and $\phi = 1.1$, respectively. The upper, saturated K(g) profile (square markers) in Fig. 2(a) is from the fuel-rich flame (full profile not shown), while the lower line shape (circular markers) is recorded in the fuel-lean flame. The solid lines show the curve fits to the K(g) profiles. In the fuel-lean case, the UV pulse position is close to the line center, where a low-bandwidth representation of the PF signal is clearly visible. In the optically thick, fuel-rich case, the UV pulse position was chosen further out in the wing of the line shape (dashed circle). The fully time-resolved PF signals measured with the high-bandwidth detector are shown in Fig. 2(b). The KOH molecules fragmented at $t = 0$ cause an increase in K(g) absorbance, which decays as the molecules recombine. The K(g) line shape is incorporated in the PF signal baseline to extract only the contribution of the UV pulse induced K(g) absorbance. The raw signals and more information on the curve fitting procedure can be found in Supplement 1.

Figure 3 shows typical time series of K(g) and KOH(g) concentrations (mole fractions) measured 15 mm above the plate during conversion of 260 μg and 330 μg KOH(s) at $\phi = 0.8$ and $\phi = 1.1$, respectively. As seen from the time series, there is a rather stable “plateau” region (black arrows), where the rate of KOH vaporization was fairly constant. The concentrations

Fig. 2. (a) K(g) TDLAS line shapes (full profiles not shown) measured with the low-bandwidth detector from a fuel-rich ($\phi = 1.1$) and a fuel-lean ($\phi = 0.8$) flame. A low-bandwidth PF signal is visible in the fuel-lean case. (b) K(g) decays following UV pulse-induced KOH(g) fragmentation ($t = 0$) measured with the high-bandwidth detector at $\phi = 0.8$ and $\phi = 1.1$. See Supplement 1 for raw signals and details on the curve fitting.

Fig. 3. Time series of K(g) and KOH(g) release measured 15 mm above the platinum plate. (a) Fuel-lean flame ($\phi = 0.8$) with initial KOH(s) mass of 260 μg . (b) Fuel-rich flame ($\phi = 1.1$) with initial KOH(s) mass of 330 μg . Error bars denote uncertainties of individual measurements.

quickly drop when the sample is almost completely vaporized. A higher vaporization rate was observed for fuel-rich conditions, most likely since the temperature of the plate increased with ϕ . The fluctuations in K(g) concentration are probably due to flame instabilities and small variations in equivalence ratio.

The error bars in Fig. 3(a) illustrate the total uncertainty of individual KOH(g) measurements (11% for the fuel-lean and 22% for the fuel-rich case), calculated from the uncertainties in UV pulse energy, temperature, PF signal noise, UV beam radius, and path length given above, the latter three being most significant. The detection limits for fuel-lean and fuel-rich conditions, determined from the signal-to-noise ratio (SNR, 3σ) in curves such as in Fig. 2(b), are 70 ppb (comparable sensitivity as

Fig. 4. (a) Measured amount of substance (squares) as a function of initial KOH(s) substance on the plate. Blue solid line—linear fit; dashed line—perfect correlation. Error bars denote the error bounds based on individual measurement uncertainty. (b) Initial and measured amount of substance (upper panel) and plateau concentrations (lower panel) as a function of equivalence ratio. Dashed lines—predicted equilibrium concentrations.

in Ref. [9]) and 1.2 ppm, respectively. The K(g) detection limit is 0.9 ppb, similar as in Ref. [18].

Assuming that K(g) and KOH(g) are the most abundant K species in the gas, the sum of K(g) and KOH(g) substance released during a time series should add up to the initial amount of KOH(s). Taking a pair of K(g) and KOH(g) time series and using the ideal gas law, the total amount of substance (moles), n_{tot} , is calculated as

$$n_{\text{tot}} = \frac{\pi L^2 U_f p}{4RT} \int_0^{t_m} [C_K(t) + C_{\text{KOH}}(t)] dt, \quad (2)$$

where L is the path length, U_f is the velocity of the burnt gases, p the pressure, R the ideal gas constant, T the temperature, t_m is the measurement time, and C_i denotes the K(g) and KOH(g) concentrations. A gas velocity of 1 m/s is assumed based on 1D reaction kinetics simulation using Cantera [22].

The technique is validated by closing the (mole) mass balance of K, both as a function of the initial (weighted) dry KOH(s) mass varied in the range 190–1500 μg and the equivalence ratio varied in the range 0.7–1.15. The measured amount of substance is calculated using Eq. (2) and concentration time series as exemplified in Fig. 3. The concentrations do not drop to zero at the end of the displayed time series (Fig. 3), but this is neglected, as weighing the plates after the measurements does not show any remaining KOH(s). As a second validation step, the average plateau concentrations are compared to thermodynamic equilibrium concentrations calculated with FactSage [23]. The results of the validation are summarized in Fig. 4.

Figure 4(a) shows the total K compound substance measured with PF-TDLAS as a function of the initial KOH(s) substance. Each point (red square markers) represents the evaluation of one pair of time series using Eq. (2). The blue solid line represents a linear fit and the dashed line a perfect correlation. The error bars illustrate the 1σ uncertainty of the total substance measured with PF-TDLAS and obtained using Eq. (2) with the upper and lower error bounds of the individual KOH(g) measurements in the time series [Fig. 3(a)]. The measured substance is in good agreement with the initial amount of KOH(s) substance on the plate.

Figure 4(b) summarizes the measurements as a function of equivalence ratio. The upper panel shows the total K compound substance measured with PF-TDLAS in comparison with the initial KOH(s) substance. The markers in Fig. 4(b) represent the average of three pairs of time series with approximately 300 μg of initial KOH(s). Error bars indicate the respective standard deviations. A good agreement is found between the total measured K compound substance and the initial KOH(s) substance, with an exception at $\phi = 0.8$, which we cannot explain.

The markers in the lower panel of Fig. 4(b) show the plateau concentrations (average of three) and the corresponding predicted equilibrium concentrations (dashed lines) for the different equivalence ratios. For comparison, the concentrations are normalized to the vaporization rate estimated by dividing the initial KOH(s) mass on the plate by the plateau time (Fig. 3). The measured plateau concentrations as a function of equivalence ratio are similar to the results presented in Ref. [7] and in good agreement with equilibrium calculations for fuel-lean flames. However, significant deviations from equilibrium are evident close to stoichiometry and in fuel-rich flames. This discrepancy could be explained by radical removal reactions, which deplete radicals such as oxygen hydroxyl, causing inhibition of CO oxidation and increased K(g) concentrations at the expense of KOH(g) [24].

As demonstrated in this work, KOH(g) measurements under optically thick conditions with respect to K(g) are enabled by shifting the UV pulse and PF signal away from the fragment absorption line center. However, the SNR, and thus the sensitivity of the KOH measurement, then become dependent on the background K(g) concentration and will generally be lower than under optically thin conditions. The reasons are a decreased fragment absorption cross section in the wings and a lower transmitted probe laser intensity for optically thick samples. The detection limit in the fuel-rich case could be improved by employing a high-power probe laser or a UV laser with higher pulse energy. Employing the weaker K(g) absorption lines around 404 nm [7] would shift the dynamic range towards higher concentrations and impair the detection limits, but facilitate the investigation of fuel-rich flames.

In conclusion, we present a novel method to perform photofragmentation spectroscopy, where full absorption profiles of the fragment species are measured using TDLAS. This extends the dynamic range for both target and fragment species and enables accurate quantification even at high fragment absorbance. The technique is demonstrated by detecting the reactive compounds KOH(g) and K(g) in a flat flame at around 1800 K and reaching KOH(g) detection limits of 0.07 and

1.2 ppm under fuel-lean and fuel-rich conditions, respectively, while K(g) was in the range of 0.12–16 ppm. The mass balance for the K compounds was closed over the conversion time, both as a function of initial KOH mass and flame equivalence ratio.

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See Supplement 1 for supporting content.

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