Measuring NO and temperature in plasma preheated air using UV absorption spectroscopy

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Abstract

A new fast sensor for simultaneous high temperature diagnostics (above 800 K) of nitrogen oxide (NO) concentration and gas temperature (T) was developed based on the spectral fitting of low-resolution NO UV absorption near 226 nm. The sensor was intended for process control in future low-carbon footprint heavy process industries using renewable powered electro fuels (e.g. H_2 , NH_3) or plasma torches as heat source. Due to excitation of molecular vibration, the shape of the selected NO feature, including (0, 0), (1, 1), and (2, 2) vibrational transitions of the $A^2\Sigma^+ - X^2\Pi^2$ electronic system had a strong temperature sensitivity at temperatures above 800 K. The fitting was made using the well-known NO molecular constants of the $A^2\Sigma^+ - X^2\Pi^2$ electronic system. To reduce the computational time, a library of the molecular spectra calculated at different temperatures was created. The fitting of an experimental spectrum representing the convolution of the instrument line function of the spectrometer with the molecular spectra was performed using the pre-calculated library spectra. Based on comparison with conventional measurement methods, the accuracy of the developed sensor was within 15% for NO and about 40 K for T , clearly showing the potential for fast in situ diagnostics in hot process gases.

1 Introduction

The necessity to reduce the CO_2 emissions, together with the depletion of fossil fuels, has forced the developers of high-temperature energy conversion equipment to look for alternative fuels and new (or moderated) technologies. The replacement of fossil fuels in heavy process industries' combustion processes with electro fuels (plasma torch, hydrogen) is considered a potentially attractive approach in Sweden due to the large amount of renewable electricity production from hydro and wind power. For example, in the hydrogen break through iron making technology (HYBRIT) initiative (<http://www.hybritdevelopment.com/>) and the CemZero project (<https://energyindustryreview.com/construction/>), the focus is to replace fossil fuels with electro fuels in iron, steel, and cement production. An important precondition for the replacement of fossil fuels is that the combustion/heating performance of the sustainable system would be the same and that the release of pollutants, such as NO_x , would be kept low. Unfortunately, the electro fuels might be

a source of significant NO_x emissions. For example, in pilot-scale experiments [1] comparing different renewable alternatives to fossil fuels in straight-grate induration machines, it was found that H_2 combustion results in much higher NO_x emissions than fossil oil combustion. The plasma discharge can also generate a lot of NO_x [2].

Considering the limited experience of the heavy process industry with electro fuels, fast simultaneous in situ monitoring of NO concentration and temperature at different parts of the process would be advantageous. That would allow process control in terms of efficiency and NO_x emissions, the latter using primary (e.g., burner optimization) or secondary (e.g., flue gas cleaning) methods. In this work, we report the development of an online in situ UV absorption sensor for simultaneous diagnostics of NO concentration and temperature in hot process gases ($T > 800$ K).

There are several spectroscopic techniques, both optical and laser based, for NO detection in hot environments using strong UV electronic transitions. Laser methods, such as laser induced fluorescence (LIF) [3–5], and cavity ring-down spectroscopy [6], have been applied for diagnostics of NO in flames using rotational transitions in $A^2\Sigma^+ - X^2\Pi^2$ electronic system, mainly around a wavelength of 226 nm. The methods have demonstrated good accuracy, within 10–15%, at flame temperatures. The LIF has also been used

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for deriving flame temperature by testing different rotational transitions [7]. The application of these methods to industrial processes is however hampered by the complexity and high cost of the experimental setups. Apart from UV, NO absorbs in near- and mid-IR as well (Fig. 1), for which laser diodes are now available. The cross-sections of near-infrared and mid-IR vibrational–rotational absorption transitions are lower than those of UV. The transitions also strongly overlap with the transitions of the major combustion products. This limits the application of the IR sensors to low-temperature studies. However, the relatively strong mid-IR transitions at 5300 nm have potential for high-temperature diagnostics in practical flows [8]. In contrast, electronic UV absorption transitions are stronger and have less interference with the major combustion products. For example, H₂O absorption (for 10,000 ppm, path length 100 cm, and $T=296$ K) at 225 nm is estimated to be lower than 0.002 based on the H₂O cross-sections reported in [9] for wavelengths up to 200 nm and above 290 nm. Non-expensive diode lasers emit light in the visible, or IR region. Therefore, their application for NO UV absorption requires frequency conversion to achieve the desired UV region, which makes the experimental system more complex. The development of tunable diode laser (TDL) systems, including frequency conversions steps, have been demonstrated for NO detection in cold gases [10] and in gas turbine exhausts at high temperatures [11]. The estimated uncertainty of the sensor measurements is 10%.

Another approach is to use a relatively cheap absorption system including a UV broadband source and a spectrometer. In this case, line-of-sight UV resonant absorption from a whole vibrational band (or bands) of the NO electronic transition is measured. The approach is mostly used in combination with sampling of the gas to an optical cell at fixed temperatures, see, for example [12–14]. Quantification is often made using calibration experiments. A number of investigations demonstrated line-of-sight UV absorption measurements at high-temperature conditions of a heat-pipe cell [15], flat flames [16] including high-pressure flame facility [17], turbine engine exhausts [18], SI engine [19], and shock tubes [20]. NO concentrations were generally derived by comparing the signal measured with model calculations based on the theoretical line-by-line absorption in the NO γ (0, 0) band. The quantification required flame temperature and pressure. To the best of our knowledge, no work has been made on simultaneous quantification of NO concentrations and temperature from high-temperature low-resolution UV absorption spectral profile of the feature near 226 nm. Here, we use the spectral fitting of the NO feature near 226 nm including (0, 0), (1, 1), and (2, 2) vibrational transitions for simultaneous quantification of the NO mole fraction and temperature in the hot gases ($T > 800$ K). The fitting is also used for deriving the NO mole fraction at low temperatures.

Fig. 1 Room-temperature NO (a) and H₂O (b) molecular absorption spectral calculations made using the LIFBASE [21] and HITRAN [22] databases using 100 ppm NO and 10,000 ppm H₂O and path length 100 cm. The NO spectrum is calculated from 200 to 6000 nm, the insertion in the panel a is the zoom-in UV NO absorption from 200 to 230 nm. The H₂O spectrum is shown from 950 to 6000 nm. See also the next section for more details regarding the simulations

2 Data reduction

In an absorption measurement, a signal measured by a detector that is attached to a spectrometer and tuned to the wavenumber ν_0 can be written as

$$I_m(\nu_0) = C \int_0^\infty \varepsilon(\nu) I_0(\nu) \cdot e^{-\alpha(\nu)l} \cdot \Phi(\nu - \nu_0) d\nu + I_{D.C.}(\nu_0), \quad (1)$$

where I_0 is the initial intensity of light, $\alpha(\nu)$ is the absorption coefficient of the medium at frequency ν , l is the absorption path length, $I_{D.C.}(\nu_0)$ is the dark current at wavenumber ν_0 , C is the sensitivity of the photo detector, $\varepsilon(\nu_0)$ is the quantum efficiency of the photo detector, and Φ is the normalized instrument line function of the spectrometer:

$$\int_0^\infty \Phi(\nu - \nu_0) d\nu = 1. \quad (2)$$

The absorption coefficient can be expressed as [23]

$$\alpha(\nu) = \frac{\pi e^2}{mc^2} \sum_{i,k} f_{ik} N_i \cdot \theta(\nu - \nu_{ik}), \quad (3)$$

where N_i is a population of the species in quantum state i (cm^{-3}); f_{ik} is the oscillator strength for the transition between quantum states i and k ; and e , m and c represent the stand-

$$\int_0^\infty (1 - \text{Tr}(\nu_0)) d\nu_0 = \int_0^\infty \left(1 - \exp \left(-X_M \cdot \frac{\pi e^2}{mc^2} \cdot l \cdot \frac{P}{kT} \sum_{i,k} f_{ik} \cdot \frac{g_i \cdot e^{-\frac{E_i}{kT}}}{Z(T)} \cdot \theta(\nu - \nu_0) \right) \right) d\nu, \quad (7)$$

ard fundamental constants, θ is the normalized absorption line function (cm), and ν_{ik} is the frequency for the transition between quantum states i and k (cm^{-1}). The summation in Eq. (3) should be made over all radiative transitions.

In the case of a Boltzmann distribution over the internal degrees of freedom, N_i is related to the species mole fraction X_M through

$$N_i = X_M \cdot \frac{P}{kT} \cdot \frac{g_i \cdot e^{-\frac{E_i}{kT}}}{Z(T)}, \quad (4)$$

$$\int_{\nu_1}^{\nu_2} (1 - \text{Tr}(\nu_0)) d\nu_0 = \int_{\nu_1}^{\nu_2} \left(1 - \exp \left(-X_M \cdot \frac{\pi e^2}{mc^2} \cdot l \cdot \frac{P}{kT} \sum_{i,k} f_{ik} \cdot \frac{g_i \cdot e^{-\frac{E_i}{kT}}}{Z(T)} \cdot \theta(\nu - \nu_0) \right) \right) d\nu. \quad (8)$$

where P is the pressure, T is the temperature, g_i and E_i are the degeneracy and energy of the i -th quantum state,

respectively, $Z(T)$ is the internal partition function, and k is the Boltzmann constant.

The transmittance measured by the detector attached to the spectrometer is given by

$$\begin{aligned} \text{Tr}(\nu_0) &= \frac{I_m(\nu_0) - I_{D.C.}(\nu_0)}{I_m^0(\nu_0) - I_{D.C.}^0(\nu_0)} = \frac{\int_0^\infty \varepsilon(\nu) I_0(\nu) \cdot e^{-\alpha(\nu)l} \cdot \Phi(\nu - \nu_0) d\nu}{\int_0^\infty \varepsilon(\nu) I_0(\nu) \cdot \Phi(\nu - \nu_0) d\nu} \\ &= \frac{\int_0^\infty e^{-\alpha(\nu)l} \cdot \Phi(\nu - \nu_0) d\nu}{\int_0^\infty \Phi(\nu - \nu_0) d\nu} \\ &= \int_0^\infty e^{-\alpha(\nu)l} \cdot \Phi(\nu - \nu_0) d\nu. \end{aligned} \quad (5)$$

where $I_m^0(\nu_0)$ and $I_{D.C.}^0(\nu_0)$ are the signals detected by the spectrometer when the absorption path (cell) is filled with a buffer gas with and without light source on, respectively. We assume that I_0 and ε can be regarded as constant when integrating over the instrumental bandwidth. Integrating Eq. (5) over ν_0 gives

$$\int_0^\infty \text{Tr}(\nu_0) d\nu_0 = \int_0^\infty e^{-\alpha(\nu)l} \left\{ \int_0^\infty \Phi(\nu - \nu_0) d\nu_0 \right\} d\nu = \int_0^\infty e^{-\alpha(\nu)l} d\nu. \quad (6)$$

Combining Eqs. (3), (4), and (6), and rewriting transmittance in terms of the equivalent width, we arrive at the following expression:

see also [24] as an example of the application of the equivalence width for analysis of FT-IR spectra with moderate resolution. This last equation relates the “measured” and “true” integral absorptions (the equivalent widths), being the left and right part of Eq. (7), respectively. The summation in Eq. (7) should be performed over all transitions. However, it is often possible to find a spectral region in which only a number of transitions have substantially high intensity. If this region is sufficiently large, the infinite integration limits can be replaced by the region’s lower and upper boundaries. The summation in Eq. (7) is then performed only over the transitions lying in this region:

Provided that (1) spectroscopic parameters, (2) temperature, and (3) the path length is known, the path-averaged NO

concentration can be calculated by comparing the experimental and “true” values, see for example [24]. We note that in the given approach, no information about the instrument line function of the spectrometer is needed. The method assumes that the possible contribution of neighboring spectral features is negligible in the selected frequency region ($\nu_1 - \nu_2$) and that infinite extent of the instrumental function and absorption profile does not significantly affect the equivalent width evaluation. Another approach includes fitting the experimental spectrum, described by Eq. (5), using the known spectroscopic parameters and the instrument line function of the spectrometer in the selected frequency region

Fig. 2 The NO absorption spectra calculated using the LIFBASE program for $T=300$ K (a), 800 K (b), and 1500 K (c)

($\nu_1 - \nu_2$). The approach is especially useful for evaluating the uncertainties associated with the infinite extent of the instrumental function and with the contribution of neighboring spectral features. It might also be useful for evaluating the temperature. In this work, both methods (integration and fitting) are used for evaluating the path-averaged NO mole fraction. The fitting method is also used for deriving the path-averaged temperature.

Figure 2 shows the NO absorption spectra calculated using the LIFBASE program [21] from 200 to 240 nm for three temperatures 298 K, 800 K, and 1500 K using a spectral resolution of 1 nm, which approximately corresponds to the resolution of the spectrometer used in the measurements. The shown spectral features (3 for $T=300$ K and 4 for higher temperatures) reflect the absorption in the $A^2\Sigma^+ (v'=n) - X^2\Pi^2 (v''=k)$ electronic system. The transitions occur from the ground electronic state $X^2\Pi^2$ to the upper electronic state $A^2\Sigma^+$. Each feature corresponds to one or more vibrational bands with superimposed rotational structure. For example, the (1, 0) vibrational band near 215 nm corresponds to the transition from the ground vibrational level of $X^2\Pi^2$ state to the first excited vibrational level of $A^2\Sigma^+$ state. Figure 2 includes the notations of the vibrational transitions contributing by more than 1% to the integral absorption of a feature for the given temperature. The calculations show that the spectral features broaden with temperature. The reason for that is the redistribution of the population in rotational and vibrational levels. The shown NO spectra do not exhibit any broad absorption features and could be treated in the confined spectral range(s).

3 Experimental

3.1 Experimental set-ups

A schematic of the experimental set-up for the broadband absorption measurements of NO in the UV region is shown in Fig. 3. The DC 18 kW plasma torch (PNIX-100 model) provided by Plasnix (Korea) was placed on the 3-D positioner and used as a generator of high-temperature plasma gases rich in NO (Fig. 3b). Chamber 1 (Fig. 3c) or Chamber 2 (Fig. 3d), see also below, was mounted above the plasma torch and was used for low and middle temperature (from 295 to 800 K) or high temperature (up to 1400 K) experiments, respectively. UV NO absorption measurements in various mixtures of the plasma and co-flow gases were performed using the following optical scheme: Hamamatsu L10290 UV–VIS fiber light source with a high-brightness deuterium lamp of 9 W was used as a broadband UV light source. The radiation of the lamp was collimated by a convex lens to produce a parallel beam. The parallel beam passed through Chamber 1 or Chamber 2 and was subsequently

Fig. 3 Schematic of the experimental set-ups used for NO absorption measurements (a), photo of the plasma torch (b), photo of Chamber 1 (c) and schematic of Chamber 2 (d)

focused onto an optical fiber coupled to UV–VIS range high-speed spectrometer (Ocean Optics HR2000+GC) equipped with a diffraction grating (Ocean optics, HC-1 Grating, 600 g/mm, blazed @ 300 nm). The absorption spectra were recorded with a rate of 20 spectra per s. Typically, 100–500 spectra were averaged.

Chamber 1 is a cylindrical chamber (50 cm long, inner diameter: 12.5 cm) made of steel, with a wall thickness is 0.2 cm. Chamber 1 contains inlets for co-flow gas approximately 15 cm above the plasma torch exit and two openings for UV absorption measurements. The openings have a diameter of 1 cm and are situated along a line passing through the middle of the chamber, 20 cm below the exit of the chamber. The openings were continuously flushed with N_2 jets coming from the flattened tubes located perpendicular to the optical path to prevent the escape of plasma

gases through these openings along the optical beam, which restricted the path length of the measurements to the diameter of the chamber. Chamber 1 was also used for the room temperature experiments when pure N_2 or N_2 containing NO at two concentrations (2580 ppm and 180 ppm) was directed to the chamber using the co-flow input. The plasma gas flow and electrical power were off during such the experiments. N_2 and NO mixtures were obtained from gas cylinders delivered by AGA (relative uncertainty in NO mole fraction was ~2%).

Chamber 2 is made from steel and internally lined with 5 cm ceramic fiber (isofrax 1400 blanket, Unifrax) on all sides except the surface of the plasma torch, which was only covered with a 0.5 cm ceramic fiber paper. The internal cross-section of the chamber has a square shape with a side distance of 25 cm and an internal height of 80 cm.

The outlet is circular, with a diameter of 10 cm placed centrally above the torch. The heated co-flow in chamber 2 was injected from the side by a horizontal channel with the same cross-section and lining as the main vertical chamber. The electrical heater (Leister 5000 HT) for co-flow gas preheating was mounted centrally at the far end of the side channel, at a horizontal distance of 47.5 cm from the torch center. The bottom of the lining for the main chamber, torch, and side channel is on the same level. The chamber is equipped with optical access approximately 40 cm from the top. A constant flow of N_2 was supplied to the quartz windows. The diameter of tubes/openings from the reactor to the windows for optical access is 1 cm. The value of the N_2 flow, 2 l min^{-1} , was selected (based on the sensitivity of the UV measured concentrations to the N_2 flow rate) in such a way to minimize the mixing of the cold N_2 with the hot gases outside the inner diameter of the chamber.

The homogeneity of NO concentration and temperature along the optical path of the UV beam was verified by FTIR (2000 MultiGas analyzer, MKS Instruments) and a fine wire uncoated S type (Pt–Pt/10% Rh) thermocouple (TC), respectively. The variations in NO concentrations and temperature along the optical path during the experiments with the fixed plasma power were typically within 3%. The TC had 50 μm thick wires and a junction diameter of 150 μm . We chose an uncoated thermocouple with low emissivity of the junction to reduce the emissivity correction. No radicals which could initiate heterogeneous chemistry/catalytic effects were expected at the location of the measurements due to the relatively low gas temperatures ($T < 1350 \text{ K}$). The radiation correction was estimated similarly to [25]. The emissivity of the junction at a given temperature was assumed be the same as the emissivity of platinum, reported by [26], (about 0.16 for clean Pt at $T = 1300 \text{ K}$). The maximum temperature correction for the conditions studied in this work was about 24 K.

3.2 Experimental procedure and data handling

During room temperature experiments with the mixtures of NO and N_2 , we first measured the intensity of the radiation after passing the absorption chamber filled with pure N_2 , which gave us a reference signal. Subsequently, as the calibrated mixtures of NO and N_2 were fed through the chamber, the intensity of the radiation that passed the cell was measured again, providing a transmitted signal. In high-temperature plasma experiments, the transmitted signal was measured in the hot mixture of preheated air or N_2 and plasma gas (air or N_2). Then the plasma power was turned off, and the I_0 signal was measured in the air/ N_2 mixture while it was still hot. The transmittance measurements were started when the FTIR showed negligible concentrations of NO in the exhaust gases. The dark current (signal observed without illumination) was measured after each of the reference and

Fig. 4 Transmission spectrum of 2580 ppm NO in N_2 (blue) at 296 K, transmission spectrum of pure N_2 (red) and dark current spectrum (green)

Fig. 5 The experimental absorbance spectrum of 2580 ppm NO in N_2 at 296 K. The vertical lines mark the spectral region (near 226 nm) selected for integration. The symbols in the figure represent the measured value

transmission measurements and subtracted from the measured intensities.

As an example of the recorded spectra, Fig. 4 shows the intensity of the light after passing Chamber 1 flashed with pure N_2 and N_2 with NO addition. The NO addition is 2580 ppm. The dark current is included in the figure. The spectrum plotted as an absorbance $[1 - \text{Tr}(\nu)]$ is shown in Fig. 5.

To determine the NO concentration, a computer code was written that calculated the theoretical absorption spectrum using Eq. (8). As in [27], the spectral line parameters needed for calculations of the NO mole fractions were taken from [21, 28]. The NO internal partition function $Z(T)$ was calculated using tabulated thermodynamic data [29]. The normalized absorption line function was simulated using the Voigt profile [30] calculated by the algorithm suggested by Humlíček [31]. The spectral region including the vibrational transitions (0, 0),

(1, 1), and (2, 2), roughly between 220 and 230 nm (the region marked by vertical lines in Fig. 5), was chosen as the integration interval for deriving absolute values of the NO mole fraction. The choice was governed, on one hand, by the high signal to noise ratio for the (0, 0) feature in comparison with those for (0, 1) and (0, 2) resulting from a steep gradient in both the emission intensity of the Hamamatsu L10290 lamp source and the grating transmittance properties in the region of the NO absorption feature. On the other hand, the selected band contained transitions from higher than 0 vibrational levels. This circumstance lead to pronounced dependence of the feature shape on temperature, which can be beneficial for deriving the temperature using spectral fitting. The relatively low left boundary value of 220 nm for the selected feature was selected to cover high-value rotational levels and vibrational transitions (1, 1) and (2, 2), important at high-temperature applications. Figure 6 shows an example of the true simulated absorbance spectra of NO for the (0, 0) band around 226 nm at 296 K for $l = 12.5$ cm and NO concentration of 172 ppm. The figure also includes the simulation of the low-resolution broadband

Fig. 6 The true and low-resolution broadband UV absorbance spectra of NO for the (0, 0) band around 226 nm calculated at the following conditions: $T = 296$ K, $l = 12.5$ cm, and NO concentration 172 ppm

Fig. 7 Measured and fitted NO spectra at room temperature and the nominal (experimental) NO level in the mixture **a** 180 ppm and **b** 2580 ppm

UV absorbance spectrum calculated by the convolution of the true simulated absorbance spectra with the line shape of the spectrometer. For the above calculation and the fitting of the experimental spectra, we approximated the instrumental function of the spectrometer using a triangular instrumental line shape [32] with 1.1 nm resolution (see next section).

It is also important to discuss a possible overlap of the selected feature with features of other molecules. In the high-temperature experiments performed in this work, the plasma was used to heat the air. Plasma can be a source of a significant amount of NO_2 [33] whose UV absorption features overlap with the selected NO transitions. The UV and visible absorption NO_2 cross-sections are accurately known with a very good spectral resolution at room temperature [34]. Therefore, in the case, if both NO and NO_2 are present in the room temperature mixture, the concentration of NO and NO_2 could be derived from the measured absorption spectra by fitting the calculated and the experimentally determined absorption spectrum, similar to the method developed in [35] for H_2S , NO_2 , and SO_2 . At high temperatures, which are targeted at this work, the application of a similar method is complicated, since the temperature dependence of the UV NO_2 cross-section is poorly known. In [36], the effect of temperature on the NO_2 absorption cross-sections at several fixed wavelengths in the UV and visible spectra was measured. It was found that for some wavelengths in the UV region, a sharp non-monotonic temperature dependence exists. In the visible part of the spectra (see also [37]), broadening of the bell-shaped feature and smoothing of the superimposed spectral fluctuations were noticed. We will continue to discuss the spectral overlapping of NO and NO_2 in Sect. 4.

4 Results and discussion

At first, let us consider the room temperature experiments with the mixtures of N_2 and NO. The experimental spectrum shown in Fig. 5 was integrated into the chosen boundaries.

The obtained values were compared with the calculations made using Eq. (8). The left and right sides of the equation equaled each other at an NO concentration of 2485 ppm which is within a few percent from NO concentration in the N₂/NO mixture. The comparison of the experimental integrated absorption measured in the case when N₂ contained NO at 180 ppm with the theoretical one resulted in a NO concentration of 172 ppm (Fig. 6). The true molecular spectrum calculated at 296 K was used as an input for fitting. The fitting parameters were the NO mole fraction, the background, and the resolution of the spectrometer. Figure 7 shows the experimental and fitted spectra plotted as $1 - T$ for 180 ppm and 2580 ppm of NO mole fraction. The fitted NO values are 182 ppm and 2571 ppm.

To test if the above described broad band absorption methodology can be applied for determining NO mole fractions at high temperatures, we performed absorption measurements of the NO mole fraction in the hot plasma generated environment using Chamber 1 and Chamber 2. A summary of the performed measurements is shown in Table 1. The NO mole fraction and the temperature in the hot mixtures were measured using FTIR and the fine wire TC, respectively. The FTIR measurements indicated the presence of non-negligible NO₂ concentrations ranging from 5 to 12% of the total NO_x (NO + NO₂) mole fractions in all measured cases. In general, NO₂ concentration increased with total NO_x concentration. As a typical example, Fig. 8 shows the measured UV absorbance spectra for Case 12 (Table 1, FTIR NO = 6150 ppm, NO₂ = 660 ppm, TC T = 1160 K). The figure includes the calculated NO₂ spectrum (NO₂ = 660 ppm, l = 25 cm). The simulations

Fig. 8 The measured UV absorbance spectrum for Case 12, NO = 6150 ppm, and the calculated NO₂ absorbance spectrum (NO₂ = 660 ppm, l = 25 cm), see text for more details

were performed using the methodology discussed in [35]. Since NO₂ absorption cross-sections at high temperatures are known only at a small number of the wavelengths, we performed the simulations using readily available room temperature NO₂ cross-sections [34] divided by a factor 1.2. The factor was evaluated by comparison of the NO₂ absorption cross-section at 226.4 nm for two temperatures, 293 K and 1160 K. The value at 293 nm $4.9 \times 10^{-19} \text{ cm}^2$ was taken from [34], while that at 1160 K $4.1 \times 10^{-9} \text{ cm}^2$ was approximated from [36].

As can be seen in Fig. 8, the UV experimental spectrum does not contain a clear indication of the NO₂ features at the given temperature (1160 K). We also do not observe a

Table 1 Experimental (room-temperature calibrated mixture and FTIR measurements) values and values evaluated based on the integration and fitting procedures the NO mole fraction

No.	Path length (cm)	T (K)	Experimental NO (ppm)	Integrated NO (ppm)	Fitted NO (ppm)	Deviation (integrated) (%)	Deviation (fitted) (%)
1	12.5	298	180	172	182	4.4	- 1.1
2	12.5	298	2580	2485	2571	3.7	0.3
3	12.5	613	686	662	664	3.5	3.2
4	12.5	704	1095	1063	1076	2.9	1.7
5	12.5	714	1571	1485	1534	5.5	2.3
6	12.5	740	1485	1441	1522	3.0	- 2.5
7	12.5	840	2480	2386	2429	3.8	2.1
8	25.0	580	2075	1839	1800	11.4	13.2
9	25.0	778	3921	3544	3507	9.6	10.6
10	25.0	943	3640	3220	3303	11.5	9.3
11	25.0	1028	5900	5656	5678	4.1	3.8
12	25.0	1160	6150	5335	5919	13.2	3.8
13	25.0	1188	5410	5016	5021	7.3	7.2
14	25.0	1251	4560	4096	3989	10.2	12.5
15	25.0	1346	6200	5635	5654	9.1	8.8

Measurements were performed in two experimental chambers. Path lengths of the measurements in Chamber 1 and 2 were 12.5 and 25 cm, respectively

bell-like shape characteristic for the visible part of the spectrum (not shown). In all experimental conditions encountered in this work, we could not observe any clear indication of NO_2 features in the measured spectra. A possible explanation of the above is that NO_2 is formed mostly during sampling of the $\text{O}_2\text{--N}_2$ mixture (containing significant NO levels) to the FTIR cell. In this case, the broadband signal can be caused by the wavelength-dependent stirring of the optical beam. It is also possible that some NO_2 is present in the mixture; however, its spectral features are considerably smoothed. In any way, for the data treatment, the broadband

signal can be considered as the background in the evaluation of the experimental spectra.

Figure 9a, b, and c shows the examples of the experimental and fitted spectra for temperatures of 714 K, 943 K, and 1160 K, respectively. The path length was 12.5 cm for the data shown in Fig. 9a, and 25 cm for the data in Fig. 9b, c. The NO values measured by FTIR are also reported. The fitting parameters were the NO mole fraction and the background. The resolution of the spectrometer was fixed to the value obtained from the fitting of the room temperature spectra, 1.1 nm.

The results reported in Table 1 show that both applied methods provide values within 13% from the nominal data for all studied temperatures. It is worth noting that the agreement is better than 6% in the case when the experiments were performed in Chamber 1. For Chamber 2, the agreement is around 10%. The possible explanation might be the larger uncertainties in the path length of the measurements for Chamber 2. In the experimental set-up including Chamber 1, the path length was very close to the diameter of the chamber due to the arrangement of the flashing N_2 jet, see Sect. 3.1. In the setup including Chamber 2, N_2 was flashed through the optical shoulders along the laser beam. Though the N_2 flow was kept relatively low (around 2 l min^{-1}), the intrusion of the flows from both optical shoulders into the flow of the hot gases inside the chamber could cause a small reduction of the path length inside the hot gases. If the actual path length was shorter than that used in the procedure of the data treatment, the measured NO level is bound to be lower than the actual one. If we assume that all NO_2 measured by FTIR was converted from NO during the probing, the agreement will worsen by approximately 7–8%.

In the frame of the work, we also attempted to derive NO mole fraction and temperature by fitting the high temperature ($> 800 \text{ K}$) NO absorption spectra near 226 nm.

Fig. 9 Measured and fitted NO spectra at $T=714 \text{ K}$, $l=12.5 \text{ cm}$ (a), 943 K , $l=25 \text{ cm}$ (b), and 1160 K , $l=25 \text{ cm}$ (c). The Experimental NO mole fraction measured using FTIR

Fig. 10 Fitted NO mole fraction and the absolute difference between the experimental and the fitted absorbance spectra at $T=1188 \text{ K}$. The experimental NO mole fraction was measured using FTIR

To reduce the computational time, we created a library of molecular spectra calculated from 800 to 1500 K with a step of approximately 25 K. The fitting of an experimental spectrum was performed using all pre-calculated library spectra. The spectrally integrated absolute residual between the experimental and the fitted data was calculated for each fitting temperature. The NO mole fraction and temperature from the fitting with the minimal integrated absolute residual were considered as the best-fitted values. To give an example of the accepted routine, Fig. 10 shows the integrated absolute residual and NO mole fraction obtained by fitting the experimental spectrum corresponding to Case No 13 (Table 1) as a function of temperature. The best fit is at 1200 K. The derived NO mole fraction at this temperature was 5261 ppm. The NO and T values are in excellent agreement with the measured ones. Table 2 summarizes the results of the fitting of the experimental spectra corresponding to Cases 7 and 10–15 in Table 1. We also estimated, based on the analysis of the simulated spectra, the sensitivity of the integrated NO feature, and therefore also, the NO mole fraction to temperature. It appeared that above ≈ 1000 K, an increase of the input temperature by 100 K results in a decrease in the NO mole fraction by approximately 10%. The effect increases at low temperatures.

To demonstrate the applicability of the developed method for online diagnostics of high-temperature gases with relatively high NO content, real-time NO mole fractions and temperature (T) were measured using NO UV absorption in a mixture of plasma gas and co-flow air (Fig. 11a). The measurements were performed using Chamber 2. Data were collected every second; 20 spectra were averaged and then fitted. Variations in NO mole fraction and T in the mixture was obtained by varying the electrical power to the plasma torch. The measured NO mole fraction was contrasted with the FTIR data, while T was contrasted with the thermocouple (TC) values. Figure 11b shows the relative difference between NO FTIR and UV absorption and the absolute difference between the temperatures measured by UV absorption and TC. Figure 11a, b shows a very good agreement between the temperatures obtained by fitting the collected

Fig. 11 Real-time NO concentration and temperature measured by UV absorption and conventional techniques in a mixture of plasma gas and co-flow air (**a**), the relative difference between NO concentrations measured with FTIR and UV absorption and the absolute difference between the temperatures measured with a thermocouple and UV absorption (**b**)

absorption spectra and by thermocouple measurements. The NO mole fraction obtained by NO UV absorption follows the NO mole fraction obtained by FTIR very well. There is, however, a 5–15% difference between them. The larger variation in the NO mole fraction measured by UV absorption than that by FTIR is explained by the fact that FTIR integrates the concentration over some effective time (several seconds for the set up used in this work) dependent, among others, on to the volume of FTIR optical cell. This integration also explains the relatively big differences

Table 2 Experimental and fitted NO mole fraction and temperature for high-temperature ($T > 800$ K) cases

No.	Path length (cm)	Exp T (K)	Exp NO (ppm)	Fitted T (K)	Fitted NO (ppm)	Deviation NO (%)	Deviation T (K)
7	12.5	840	2480	740	2047	17	100
10	25.0	943	3640	890	3167	13	53
11	25.0	1028	5900	1032	5786	1.9	− 4
12	25.0	1160	6150	1100	5620	8.6	60
13	25.0	1188	5410	1200	5261	2.8	− 12
14	25.0	1251	4560	1234	4056	11.1	17
15	25.0	1346	6200	1350	5979	3.6	− 4

between the UV absorption and FTIR data at the moments when the power to the plasma torch was changed. Defining the detectable limit as the mole fraction giving an absorption of the same magnitude as the noise, we used a single-scan spectra (not shown) to estimate a single-scan detectable limit of ~ 150 ppm for NO for the current setup ($T > 1000$ K, $l = 25$ cm). According to Directive 2010/75/EU [38], emission limit values for NO_x for combustion plants using solid or liquid fuels is about 150 ppm of NO for total rated thermal input between 100 and 300 MW. Provided that a 1–2 s acquisition time is acceptable for monitoring purposes, the sensitivity of the measurements will be on the order of 15 ppm m^{-1} . We note that there is a significant potential for sensitivity improvement. For example, a more powerful UV lamp as well as spectral grating and optical fiber with better transmittance properties in the region of the NO absorption feature can make it possible to obtain spectra with much better signal to noise ratio. We note that the developed method demonstrated a good accuracy in the range of studied NO optical densities, up to few thousand ppm of NO per meter at atmospheric pressure and elevated temperature. At higher pressure or NO column density, some modification of the method will eventually be needed to account for saturation in the absorption molecular lines [39]. The studied range of NO optical densities is deemed to be sufficient for most of the practical atmospheric pressure systems.

5 Conclusion

A new strategy for quantitative broadband UV absorption diagnostics of the NO mole fraction and temperature (T) using tabulated NO molecular constants is described. Using NO spectroscopic parameters, we performed spectral fitting of the feature at 226 nm recorded at low spectral resolution for quantification of the NO mole fraction and T . Spectral fitting of both NO mole fraction and T worked best at $T > 900$ K, when high-temperature transitions (1, 1) and (2, 2) contribute noticeably to the spectral shape of the feature. Furthermore, the NO concentration was derived by a comparison of the values of the equivalent width of the selected NO feature determined from the measured UV spectra with those calculated from the simulated NO molecular spectra. The accuracy of the methods for quantitative diagnostics is demonstrated by comparison of the calculated/fitted values of the NO mole fraction and T with those measured using conventional techniques (FTIR and thermocouple).

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