

Towards an Optogalvanic Flux Sensor for Nitric Oxide Based on Rydberg Excitation

Patrick Kaspar¹, Fabian Munkes¹, Yannick Schellander¹, Joshua Fabian¹, Malte Kasten¹, Luana Rubino¹, Denis Djekic², Patrick Schalberger³, Holger Baur³, Robert Löw¹, Tilman Pfau¹, Jens Anders², Edward Grant⁴, Norbert Frühauf³, and Harald Kübler^{1,*}

¹5th Institute of Physics, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

²Institute of Smart Sensors, University of Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany

³Institute for Large Area Microelectronics, University of Stuttgart, Allmandring 3b, 70569 Stuttgart, Germany

⁴Department of Chemistry and Department of Physics & Astronomy, The University of British Columbia, 2036 Main Mall, Vancouver, BC Canada V6T 1Z1 Vancouver, Canada

*h.kuebler@physik.uni-stuttgart.de

Abstract: We report three-photon continuous-wave laser excitation of nitric oxide to high lying electronic Rydberg states and its conversion into a detectable current in the nA regime using our optogalvanic trace-gas sensor prototype. © 2021 The Author(s)

1. Introduction

The exact determination of small concentrations of nitric oxide (NO) is crucial in a variety of applications. These applications comprise the control of crop growth [1, 2], or combustion processes [3], as well as the production of exact gas mixtures for the semiconductor industry [4]. Furthermore, medical investigations of inflammatory diseases like asthma [5], or cancer rely on the exact analysis of NO in human breath [6].

The sensing scheme we propose is based on Rydberg excitation and subsequent collisional ionization. Fig. 1a shows the sensor's working principle allowing the detection of NO in a background gas in through-flow based on a three-photon excitation scheme using continuous-wave (cw) laser systems. The target state being a Rydberg state eases ionization due to its vicinity to the first ionization limit of NO (9.26 eV) [7]. A voltage of 1 – 10 V separates these charges and guides them to the electrodes. A trans-impedance amplifier (TIA) then amplifies the current and converts it into a voltage. The measurement can be performed in ml-sized volumes. A previous publication [8], involving a two-photon excitation scheme and using pulsed lasers already demonstrated this technique, however the presented cw excitation shown here increases the selectivity as well as the bandwidth.

2. Results

For first current measurements NO with a purity of 99.5 % was used at a constant flow through the cell. The flow is controlled with a mass flow controller and the pressure inside the cell is monitored.

The $H^2\Sigma^+$ and the $H^2\Pi$ electronic state are lying very close to each other which results in a perturbation between themselves and adjacent states, yielding a very complex energy level structure [7]. Therefore, the lasers were tuned to a known excitation path given by Ogi, et al. [9]. The first transition is part of the P_{12} branch with ($J_X = 5.5$) starting from the $X^2\Pi_{3/2}$ spin-orbit component of the ground state to the $A^2\Sigma^+$ electronic state. The transition wavelength is 226.97 nm. This transition can be detected by optical absorption spectroscopy and verified with a simulation using the program *pgopher* [10]. The transition from the $A^2\Sigma^+$ to the $H^2\Sigma^+$ state is driven via the R_{11} branch with $J_A = 4.5$ at a wavelength of 540.46 nm by the green laser. Being a dipole-forbidden transition [11], and therefore having only a weak optical signature the signal could only be resolved electrically, example in Fig. 1b. The obtained signal was in the range of 500 pA. A transition to a Rydberg state was found by scanning the red laser around 834.91 nm. The detected current of almost 30 nA measured at maximum laser power clearly indicates the potential of the presented sensor prototype. The sensor's selectivity is mainly based on the three photon excitation scheme, which is unique to this particular molecule and can be seen as its "molecular fingerprint".

Photoelectrons from the electrodes as well as two photon ionization of the molecule lead to additional unwanted contributions to the current signal, visible as a constant offset. These effects may decrease the sensor's selectivity but do not influence its sensitivity. With the measured current of 30 nA at 0.5 mbar a quantum efficiency on the order of 10^{-4} can be estimated at a bandwidth of 1 kHz. Compared to the proof of principle experiment reported in [8], at a bandwidth of 10 Hz this is an increase of a factor of 10 for sensitivity per $\sqrt{\text{Hz}}$ and a factor of 100 for the temporal resolution.

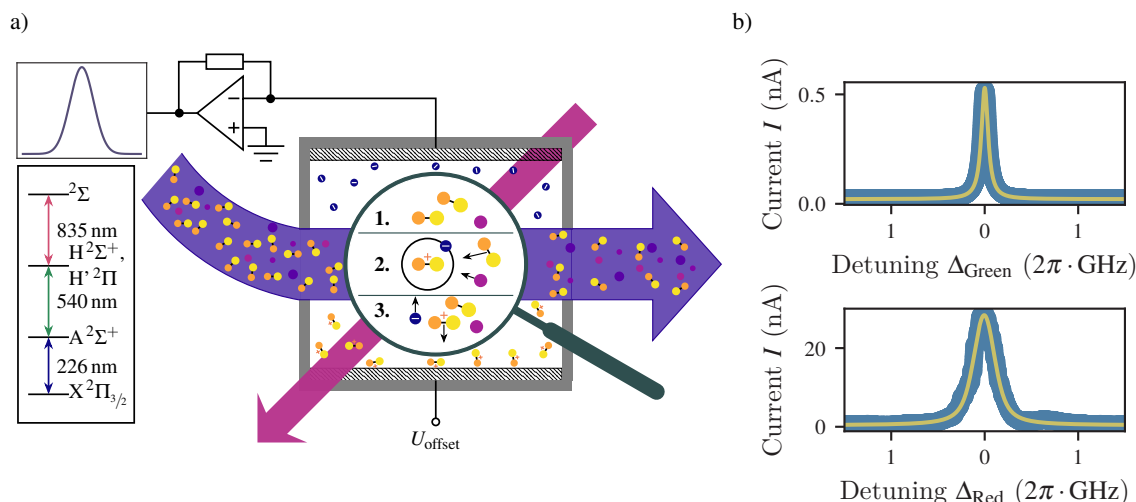


Fig. 1: a) Sketch of the sensors working principle. First an unknown gas mixture of NO enters the cell. Second: The NO is excited to a Rydberg state according to the scheme on the left. Third: The excited NO is ionized by collisions with the background gas. The applied voltage U_{offset} guides the free charges to the electrodes. A current is detected.

b) Current signal of the two-photon spectroscopy plotted versus the detuning (top panel) and three-photon spectroscopy (bottom panel). The data is plotted in blue and fitted with a Voigt fit (yellow line). The data was taken at a pressure of 0.63 mbar (top) and 0.5 mbar (bottom).

The next steps in the development of the sensor prototype are to assign the exact molecular transitions with a simulation and to start measurements with well defined mixtures of NO and a background gas like nitrogen. Further improvement will be achieved by exchanging the commercial amplifier with a custom designed monolithic trans-impedance amplifier tailored to the needs of the experiment which will be directly bonded to the gas cell.

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