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macQsimal

Miniature Atomic vapor-Cell Quantum devices for SensIng and Metrology AppLications

Deliverable D8.4

Test of NO detection with real exhaled gases

WP8 - Rydberg gas sensors

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Contents

Abbreviations

CO2	Carbon dioxide
CW	Continuous wave
H20	Water
N2	Nitrogen
NO	Nitric oxide
NO2	Nitrogen dioxide
O2	Oxygen
O3	Ozone
UV	Ultraviolet

Short names of macQsimal consortium members

accelCH	accelopment Schweiz AG, CH
BOSCH	Robert Bosch GmbH, DE
STUTT	Universität Stuttgart, DE

Executive Summary

The detection of NO relies on a selective three photon excitation of NO to a Rydberg-state and no other component of the exhaled breath. A crucial role plays here the narrowband excitation with cw-lasers, well below the Doppler-broadening of a thermal gas at room temperature. The second important point is the usage of a three-step excitation. Even if the UV-photon of the first excitation step would lead to a fragmentation of a molecule into charged particles, we can filter this background by a lock-in technique.

As we were unable, due to technical problems, to perform first simple experimental tests on parasitic excitations of other constituents, we mitigated this deliverable to a review of relevant gases. This is done by an extended literature on the relevant gases and how the absorb at the relevant UV wavelength, here 226nm.

Need for the deliverable

This deliverable is needed to understand the response of real exhaled breath and what kind of parasitic signals may arise. If the background signal is not too large it can be filtered out by a lock-in technique. If some constituents produce a too large signal, additional measures have to be taken, like filtering these gases out or chemically altering them.

Objectives of the deliverable

The original objective was to insert real exhaled breath into our measurement setup. As we do not want to contaminate this reference setup, we have to duplicate the gas flow setup for this purpose. A deliverable is to measure the background current of the exhaled breath with the laser being detuned from any transition in the NO-molecule. This can then be benchmarked with comparable densities in a NO-N2 mixture. Due to technical problems the deliverable is mitigated to a theoretical survey. Nevertheless, this experiment will be performed anyway in the near future, as it is a crucial step to understand the potential performance of our sensing scheme.

1 Introduction

This deliverable presents a survey of the relevant gases in exhaled breath and their absorption at the spectroscopic relevant wavelength of 226nm. Most gases seem to be not a problem, which is also evident from the experimental setting so far. The 226nm runs through air for several meters and we do not observe any substantial absorption. From this we can deduce that at least on the ppm level we will not be bothered by parasitic absorptions. This survey helps to get an idea what compound could be an obstacle when trying to reach ppb level. Besides ozone we have not found a strong absorber at 226nm.

2 Outcomes

2.1 Inorganic gases

To start with, we first have a look at the composition of the atmosphere. We can immediately rule out all **noble gases**, as the excitation to the first excited state requires wavelengths of 58nm (Helium) to 179nm (Radon), well below our 226nm.

Table 1. This table (taken from the lecture "Atmospheric Sciences 321 - Science of Climate" by Professor Dennis L. Hartmann, Department of Atmospheric Sciences, University of Washington) shows an overview of the gases in our atmosphere. The concentration changes slightly, when the air is exhaled, as e.g., CO2 is increased and O2 is decreased by roughly 1%.

Table 1.1 Composition of the atmosphere.

CONSTITUENT	CHEMICAL FORMULA	MOLECULAR WEIGHT ($^{12}C=12$)	FRACTION BY VOLUME IN DRY AIR	TOTAL MASS (gm)
Total atmosphere		28.97		5.136×10^{21}
Dry air		28.964	100.0 %	5.119×10^{21}
Nitrogen	N_2	28.013	78.08 %	3.87×10^{21}
Oxygen	O_2	31.999	20.95 %	1.185×10^{21}
Argon	Ar	39.948	0.934 %	6.59×10^{19}
Water vapor	H_2O	18.015	variable	1.7×10^{19}
Carbon dioxide	CO_2	44.01	353 ppmv*	$\sim 2.76 \times 10^{18}$
Neon	Ne	20.183	18.18 ppmv	6.48×10^{16}
Krypton	Kr	83.80	1.14 ppmv	1.69×10^{16}
Helium	He	4.003	5.24 ppmv	3.71×10^{15}
Methane	CH_4	16.043	1.72 ppmv*	$\sim 4.9 \times 10^{15}$
Xenon	Xe	131.30	87 ppbv	2.02×10^{15}
Ozone	O_3	47.998	variable	$\sim 3.3 \times 10^{15}$
Nitrous oxide	N_2O	44.013	310 ppbv*	$\sim 2.3 \times 10^{15}$
Carbon monoxide	CO	28.01	120 ppbv	$\sim 5.9 \times 10^{14}$
Hydrogen	H_2	2.016	500 ppbv	$\sim 1.8 \times 10^{14}$
Ammonia	NH_3	17.03	100 ppbv	$\sim 3.0 \times 10^{13}$
Nitrogen dioxide	NO_2	46.00	1 ppbv	$\sim 8.1 \times 10^{12}$
Sulfur dioxide	SO_2	64.06	200 pptv	$\sim 2.3 \times 10^{12}$
Hydrogen sulfide	H_2S	34.08	200 pptv	$\sim 1.2 \times 10^{12}$
CFC-12	CCl_2F_2	120.91	480 pptv*	$\sim 1.0 \times 10^{13}$
CFC-11	CCl_3F	137.37	280 pptv*	$\sim 6.8 \times 10^{12}$

(Data excerpted with the permission of the Macmillan Company from *Evolution of the Atmosphere* by J. C. G. Walker, © 1977 by Macmillan Publishing Company; Verniani, 1966 © American Geophysical Union; and Williamson, 1973.) * Values of trace constituents valid in 1990 (ppmv=10^{-6}, ppbv= 10^{-9}, pptv=10^{-12}).

Nitrogen N2

Nitrogen has quite a large bandgap of more than 15eV (83nm) and will not be excited. The 226nm laser corresponds to 5.49eV and could lead to ro-vibrational excitations in the X-state. But this state is stable and with the lower energy photons of excitation step #2 and #3 we will not reach any electronic excited state.

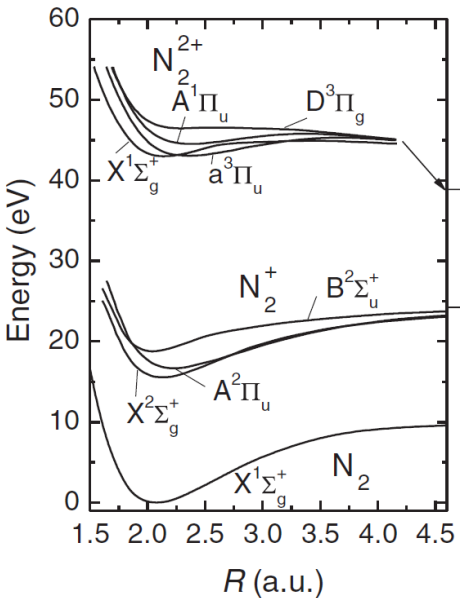

Figure 1. Level scheme of N2 taken from S. De, et. al., PHYSICAL REVIEW A 84, 043410 (2011).

Oxygen O2 and ozone O3

As shown in Figure 2, the cross-section of oxygen drops above 200nm and can probably be ruled out. On the other hand, O3 has a substantial higher cross-section, and the concentration of Ozone can be 100ppb and higher. But it seems also that the excited states of Ozone dissociate to neutral O2 +O (J. Phys. Chem. A 101, 6577-6582 (1997).

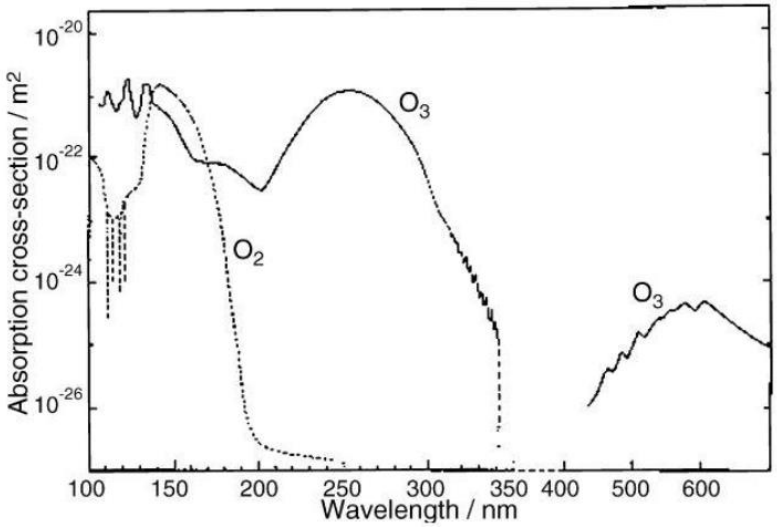

Figure 2. Cross-section of oxygen and ozone. (Data taken from Campbell, I. M. 1986. Energy and the Atmosphere: A Physical-Chemical Approach. Second Edition. John Wiley & Sons Ltd). The absorption for O2 drops above 200nm and can be ruled out to produce a severe background in our sensing scheme. On the other hand, O3 has a substantially higher cross-section, and the concentration of ozone can be 100ppb and higher. But it also seems that the excited states of ozone dissociate to neutral O2 +O (J. Phys. Chem. A 101, 6577-6582, 1997).

Water H20

Water is certainly a complicated candidate as it has a plethora of lines due to its many degrees of freedom and it has a quite large abundance. We were not able to find out whether there is a metastable state at an excitation energy at 226nm, which could lead to ionic fragments. On the other hand, the plot in Figure **3** shows that the cross-section of H2O is quite small in 226nm. We do not see any additional absorption of our 226nm laser, which runs through a normal atmospheric background for roughly one meter.

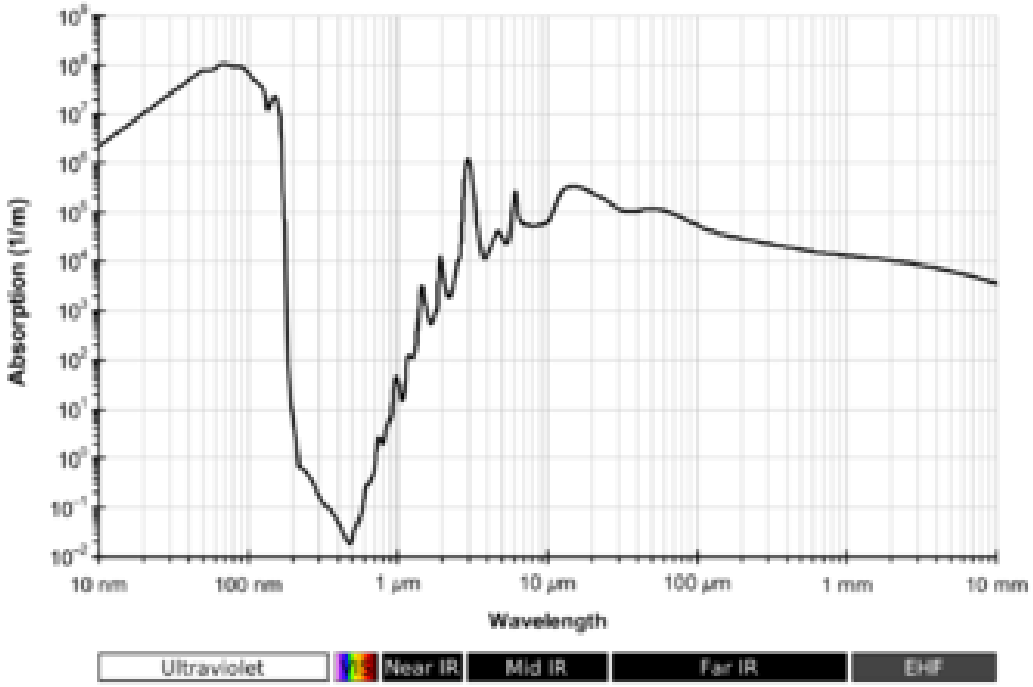

Figure 3. Absorption profile of water (source: Wikipedia).

Nitrogen dioxide NO2

As we have already seen in our experiments, we do not see any absorption in our sealed NO cells, after some time, as the NO has reacted to NO2 and N2.

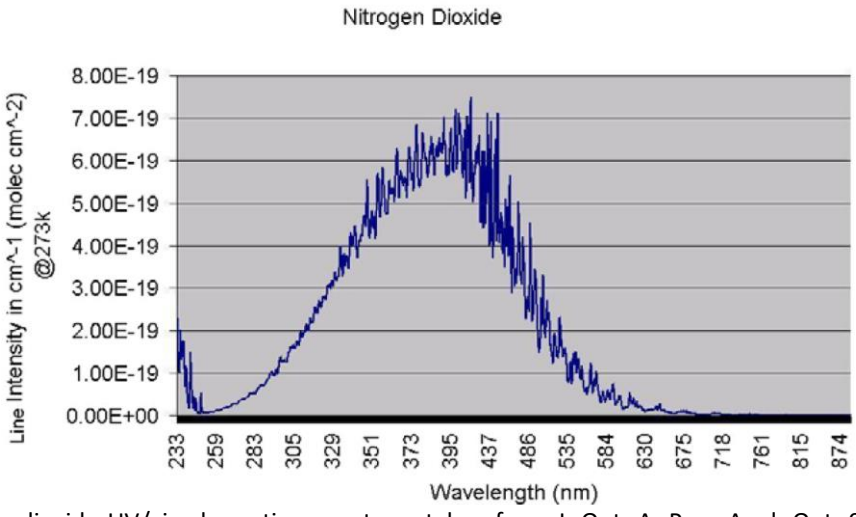

Figure 4. Nitrogen dioxide UV/vis absorption spectrum taken from J. Opt. A: Pure Appl. Opt. 9 (2007) S12–S18, http://dx.doi.org/10.1088/1464-4258/9/6/S03.

Carbon dioxide CO2

The absorption cross section of CO2 is very small and therefore negligible for our experiments

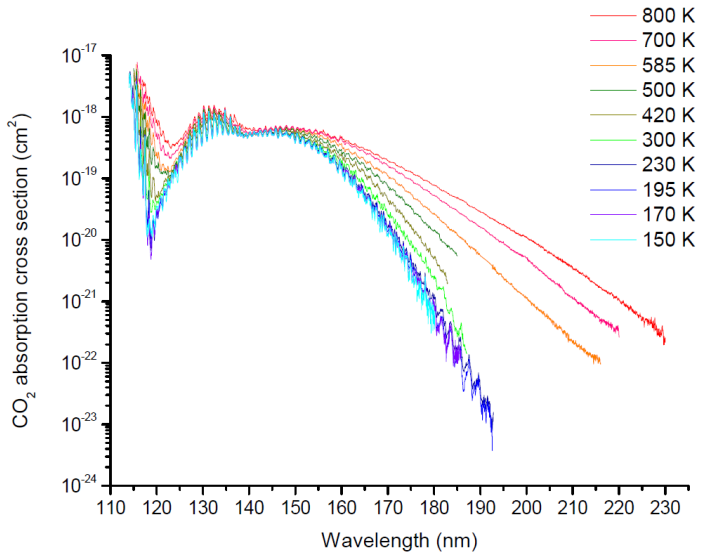

Figure 5. The absorption of CO2 as a function of temperature taken from A&A 609, A34 (2018). At room temperature the absorption cross section was not measurable in the cited article.

Overview of the absorption of atmospheric gases

it is evident that the biggest contributions at 226nm are expected from O2 and O3.

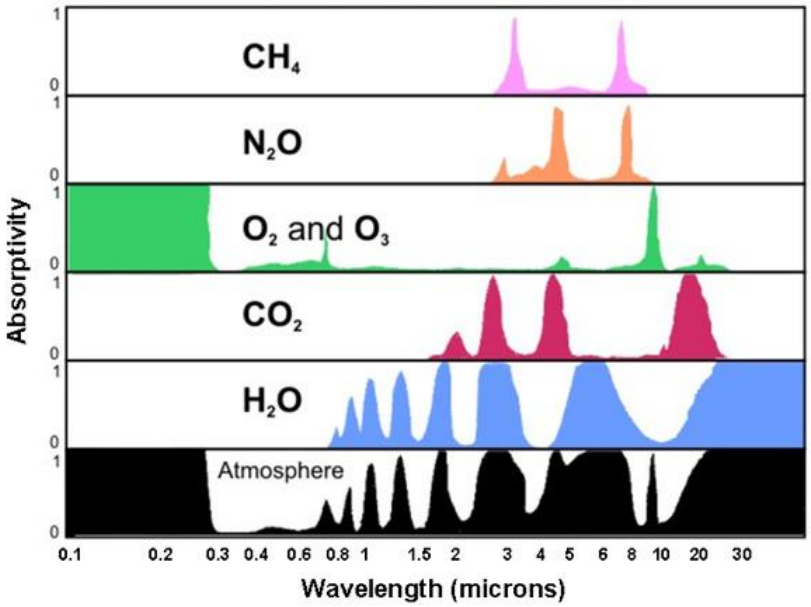

Figure 6. Overview absorption of relevant gases in the atmosphere taken from "Recent Advances in Climate Change Research: Part VIII - How Carbon Dioxide Absorbs Earth's IR Radiation (08/2020)" from www.geoexpro.com.

2.2 Volatile organic compounds in exhaled breath

Besides the atmospheric gases one finds also numerous organic molecules in exhaled breath. These molecules can exist as single molecules, but also as compounds or solved in small droplets of water.

Table 2. List of volatile organic compounds taken from Arch. Biol. Sci., Belgrade, 66 (4), 1529-1538, 2014.

Breath VOC	Range of concentrations (per 1lof alveolar breath in μg)
Propylene	5.72×10^{-3}
1,3-Butadiene	
Ethanol	1.16×10^{-2}-6.83×10^{-4}
Acetone	1.12×10^{-2}-9.90×10^{-3}
Carbon disulfide	4.46-8.71×10^{-4}
Isopropyl alcohol	9.92×10^{-3}-5.68×10^{-4}
Tert-butyl methyl ether	11.21×10^{-1}-6.84×10^{-2}
n-Hexane	1.15×10^{-1}-5.12×10^{-3}
Vinyl acetate	2.73×10^{-1}-6.20×10^{-3}
2-butanone	2.06×10^{-1}-9.18×10^{-3}
Ethyl acetate	1.06×10^{-1}-7.51×10^{-3}
Tetrahydrofuran	8.73×10^{-2}-8.62×10^{-4}
Ciklohexane	4.85×10^{-2}-1.43×10^{-3}
Benzene	1.04×10^{-2}-6.37×10^{-4}
Heptane	1.29×10^{-2}-8.43×10^{-4}
1,4-Dioxane	4.40×10^{-1}-9.83×10^{-3}
Methyl isobutyl ketone	11.18×10^{-3}-2.65×10^{-3}
Toluene	1.81×10^{-4}-2.19×10^{-4}
n-octane	1.22×10^{-2}-4.90×10^{-4}
Methyl n-Butyl ketone	1.41×10^{-3}-1.80×10^{-4}
Ethylbenzene	3.66×10^{-2}-8.40×10^{-5}
m-Xylene	1.48×10^{-2}-1.48×10^{-2}
Nonane	91.21-9.24×10^{-1}
p-Xylene	8.42×10^{-1}-5.94×10^{-4}
o-Xylene	1.02×10^{-1}-9.87×10^{-2}
Styrene	1.00×10^{-3}-7.94×10^{-3}
n-Decane	1.76×10^{-2}-8.19×10^{-4}
1-Ethyl-4-methylbenzene	1.04×10^{-3}-6.00×10^{-4}
1,2,4-Trimethylbenzene	1.36×10^{-2}-9.83×10^{-4}
1,3,5-Trimethylbenzene	1.02×10^{-2}-8.74×10^{-4}

The behavior of these molecules and compounds under UV radiation are not throughout studied. Especially information on fragmentation into charged particles is sparse and hard to find. The concentrations of these molecules are typically quite small. The largest fraction is o-Xylene with 0.1 microgram/liter which corresponds to roughly 5ppb. This is already on the edge of our detection efficiency and will only play a minor role.

3 Next steps

What is not included in this list are larger compounds of biological materials in microscopic water droplets like aerosols. Also, the absorption of microscopic or nanosomic droplets of various liquids is not really deducible from literature. But such larger compounds can always be filtered just by size.