

An optogalvanic gas sensor based on Rydberg excitations

J Schmidt^{1,2}, Y Münzenmaier¹, P Kaspar^{1,2}, P Schalberger², H Baur²,
R Löw¹, N Fruehauf², T Pfau¹ and H Kübler¹ 

¹ 5. Physikalisches Institut and Center for Integrated Quantum Science and Technology (IQST), Universität Stuttgart, Pfaffenwaldring 57, D-70569 Stuttgart, Germany

² Institut für Großflächige Mikroelektronik and IQST, Universität Stuttgart, Allmandring 3b, D-70569 Stuttgart, Germany

E-mail: h.kuebler@physik.uni-stuttgart.de

Received 21 October 2019, revised 10 December 2019

Accepted for publication 3 February 2020

Published 31 March 2020



Abstract

We investigate the properties of a trace-gas sensing scheme based on Rydberg excitations at the example of an idealized model system. Rydberg states in thermal rubidium (Rb) are created using a 2-photon cw excitation. These Rydberg-excited atoms ionize via collisions with a background gas of nitrogen (N₂). The emerging charges are then measured as an electric current, which is on the order of several picoampere. Due to the 2-photon excitation, this sensing method has a large intrinsic selectivity combined with a promising sensitivity of 10 ppb at an absolute concentration of 1 ppm. The determination of the detection limit is limited by the optical reference measurement but is at least 500 ppb.

Keywords: trace gas sensing, thermal Rydberg atoms, collisional ionization

(Some figures may appear in colour only in the online journal)

1. Introduction

The precise determination of gas concentrations is important for a broad range of situations in everyday life. Starting from the control of combustion processes in the automotive sector [1] to well-defined and pure gas mixtures for semiconductor industry [2]. Other examples are control and survey of crop growth [3, 4], development of new medical drugs, as well as monitoring of diseases such as asthma or cancer in the exhaled human breath [5]. These are some of the reasons why the abilities of gas detectors need to increase in order to fulfill the growing demand for precision.

In fact there is no gas sensor, which is equally suited for all possible situations. One class of sensors is used for high concentrations and has a broad detection range, but suffers from the challenge of being in direct contact with the medium under consideration. Those are among others capacitive,

resistive [6–8] and gravimetric sensors [9]. Sensors facing the same challenges, but which benefit from a higher selectivity are thermo- and biochemical sensors [10], which utilize tailored surface reactions. Yet, none of these detectors reaches sensitivities, which are necessary for a breath gas analysis for nitric oxide for instance. Other highly sensitive detectors are based on optical measurements. However, they are in general very sensitive to fluctuations in the light level [11–13]. These fluctuation may not necessarily be caused by an unstable light source, but also dirt particles in the beam path might lead to false detection events. In order to reach a high sensitivity, high quality resonators have to be employed, which artificially enhance the beam path length through the medium. This comes at the expense of more maintenance effort. Until today sensitivities of ppb and below are therefore only achievable with long interrogation times on large sample volumes. Electrochemical sensors [14, 15], such as amperometric or potentiometric sensors [16] suffer from cross sensitivities. Additionally, they oftentimes need a reference to function properly as it is the case for the lambda probe. The selectivity can be regained by using appropriate filters, which comes at the cost of a larger gas volume. Like most sensors,



Original content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

which are in direct contact with the investigated gas mixture, the surface deteriorates. Hence, the properties of these sensors drift. For very precise determination of gas mixtures with high sensitivity, most often mass spectrometry is used [17, 18]. Nevertheless, achieving selectivity for molecules with the same charge to mass ratio is complex and is getting more difficult for heavier particles. In addition, the bulky size and the vacuum needed for a well-defined measurement makes the application of such a device involved. A class of sensors, which are very similar to the sensing scheme we propose, are photoionization detectors [19]. There is a large variety of applications for such detectors. Reaching from atomic and molecular spectroscopy to isotope separation [20]. Atoms of the mixture constituent under consideration are optically ionized by exciting them non-resonantly into the continuum using 2- or 3-photon transitions. The excitation efficiency is low and the direct ionization diminishes the selectivity of the scheme, because not a single transition is addressed but a continuum. Therefore, other species might also get ionized. This applies to similar schemes like REMPI as well [21].

2. Working principle

Our proposed sensing principle is based on an indirect ionization. The atom or molecule of interest is excited to a specific high-lying Rydberg state using two or more laser transitions. The Rydberg state is still bound, but collisions with other particles already at thermal energies are sufficient to ionize an atom in such a state. The successively emerging charges can then be measured as a current [22, 23]. The occurrence of a current is a clear indication of the presence of the species under consideration. Additional ionization processes like associative ionization, Penning ionization and black-body induced ionization might occur in our system [24, 25] but are negligibly small.

Due to the near-resonance 2- or 3-photon excitation the proposed sensor is immediately more selective than any optical sensor involving only one or non-resonant transitions. In the ideal case, the employed lasers show only a linewidth on the order of the Doppler width or below, which enhances the selectivity even further. Since the overall probe volume is given by the extension of our glass cells and the diameters of the lasers, both are typically on the millimeter scale, the overall volume is at most in the milliliter range. Furthermore we investigate atoms at thermal velocities of several hundreds of meters per second. These atoms are exchanged with kilohertz rates in our small probe volume. Driving all transitions in saturation circumvents detection noise due to light level fluctuations [22], a problem most optical sensors suffer from.

The current I created by the charges originating from ionizing collisions is expected to behave like

$$I_{\text{Ryd}} = e \cdot n \cdot V \cdot \varrho_{33} \cdot \Gamma_{\text{ion}}. \quad (1)$$

Here e denotes the elementary charge, n is the density of particles of the trace gas in the volume V of which only the fraction ϱ_{33} is excited to the Rydberg state. ϱ_{33} also depends on the ionization rate Γ_{ion} with which the Rydberg atoms are

ionized. Equation (1) predicts a linear behavior of the gas sensor with varying amount of the gas component of interest. Γ_{ion} is a function of the density of the background gas and can be measured in a single calibration measurement. Therefore the proposed gas sensor does not need a reference. As only the type of gas under investigation and the lasers are included in the scheme, our sensor is not expected to show drift. As a very first conservative back of the envelope estimation of the detection limit we consider a minimum detectable current of 10 pA. In order to create such a current around $6 \cdot 10^7$ ionized atoms s^{-1} are required. Since the atoms fly with a thermal velocity of at least 400 m s^{-1} across the excitation region, a volume of 1 mm^3 can be exchanged at a rate of 400 kHz. Assuming an excitation efficiency of $\varrho_{33} = 10^{-4}$ [22], around 1 million atoms have to be in a volume of 1 mm^3 in order to achieve a current of 10 pA. At room temperature this corresponds to a partial gas pressure of $6 \cdot 10^{-8} \text{ mbar}$. In a background gas pressure of 1 mbar this corresponds to a detection limit of less than 100 ppb.

One way of improving the detection limit is to enhance the excitation efficiency. The excitation efficiency depends mostly on the type of atom or molecule and the availability of high power lasers. Besides all alkali atoms, also smaller molecules such as CH_4 , CF_4 [26], CO [27], H_2S [28] or NO [29, 30] have already been transferred to high-lying Rydberg states.

Since our glass cells do not show degeneracy with a highly reactive alkali atmosphere [23, 31, 32], it is fair to assume that they withstand a broad variety of chemical vapors. Because the excitation efficiency is so important, the choice of lasers is essential. Especially when the laser power is not sufficient to drive the Rydberg population up to saturation, the detection scheme will suffer under the same challenges as an optical sensor. For small wavelengths other effects such as multi-photon ionization or the photoeffect on metals on the glass surfaces can cause problems. Nevertheless, these can be tackled by using methods of signal processing, such as Lock-in amplification. Surely, the mere amount of lasers will limit the practical usability in terms of ease of use, maintenance and portability.

The transimpedance amplifier and its' noise level is technologically demanding as well. Although high precision amplifiers with very high bandwidth and low noise levels of $10 \text{ fA Hz}^{-1/2}$ exist [33], bringing the amplifier as close as possible to the source of the current is a challenge. Amplifiers, such as thermionic diodes [34–36] and channeltrons are unfortunately not applicable to our gas sensing scheme, since the pressure ranges we are considering here are too high for those devices. Furthermore thermionic diodes would require a large volume for the space charge region. This would limit the sensor in terms of scalability. A more detailed discussion can be found in [22]. Besides these technical challenges, we also have to deal with physical issues. The first is the problem of recombination of the Rydberg created charges during their flight time towards the electrodes [30], which can be solved by sufficiently large driving fields and hence shorter flight times. The other issue are depopulating collisions of atoms in the intermediate state [37] as well as purely radiative decays

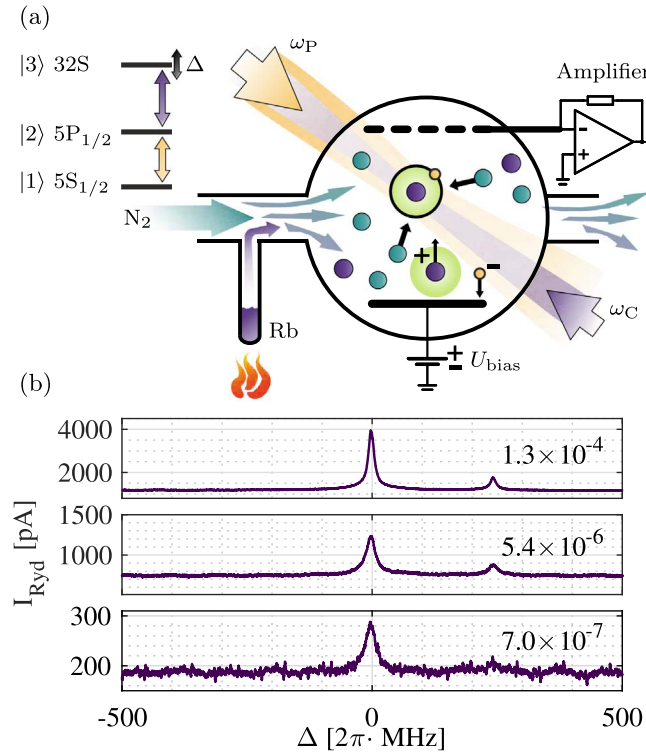


Figure 1. (a) Schematic of the experimental setup. Rb is being evaporated and diffuses through the N_2 background gas into the excitation volume. The highly excited Rydberg atoms collide with the N_2 atoms, ionize and the emerging ions are measured as a current via metallic feedthroughs. (b) Exemplary current traces for different ratios of Rb to N_2 density as function of the detuning Δ of ω_C from the Rydberg line.

of the Rydberg state [38–40]. These types of collisions depend strongly on the type of collision partner and are a source of uncertainty if one wants to investigate a completely unknown gas mixture.

3. Setup

In order to test the advantages and possible roadblocks for the competitiveness of the proposed gas detection scheme, we use Rb as a trace gas. Rb is a well investigated alkali metal, especially with regard to Rydberg physics and its' interaction with other gases is sufficiently well understood. This Rb is immersed in a background gas of N_2 , since this element does not undergo chemical reactions with Rb under the conditions considered here and interacts only little with Rb on the involved transitions. The setup consists of a glass cell similar to the ones introduced in [23, 31, 32]. The cell is filled with N_2 at a rate of $2 \cdot 10^{-6} \text{ l s}^{-1}$. At the same time Rb is evaporated from a glass manifold [41]. A schematic depiction of the setup is shown in figure 1(a). We continuously excite ^{85}Rb from the $5S_{1/2}$, $F = 3$ groundstate to the $5P_{1/2}$, $F = 2$ excited state using cw probe laser light ω_P at 795 nm with a Rabi frequency of 9.62π MHz. The intensity of the laser light is chosen such, that the population in the excited state is saturated, but yet no power broadening of the Rydberg line is

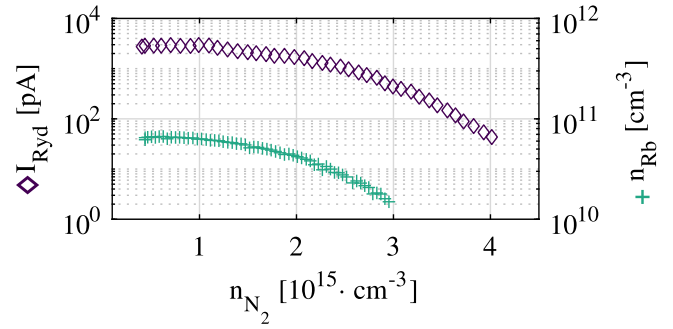


Figure 2. Amplitude of a Lorentz function fitted to the Rydberg current spectra as function of the N_2 density marked with diamonds and the ^{85}Rb density as function of the N_2 density marked with crosses on the right axis.

observable. From the excited state atoms are excited to the Rydberg state $32S$ using 474 nm cw coupling laser light ω_C with a Rabi frequency of 4.22π MHz. The $32S$ state was chosen for technical reasons. The only condition that has to be fulfilled by the Rydberg state is that the energy gap to the ionization threshold is smaller than the thermal collisional energies in the system. Due to insufficient availability of laser power no saturation can be achieved on this transition. The diameter of the coupling laser and the dimensions of the glass cell form the volume of the excitation region, which is only $8.8 \cdot 10^{-6} \text{ l}$ large. The ions emerging from the Rydberg excited atoms are guided towards the electrodes using a small bias voltage $U_{bias} = 2.6 \text{ V}$, which is still sufficiently small that no Stark shift is observable on the scale of our Rydberg linewidth. The current impinging on the electrodes is then amplified using an external transimpedance amplifier with a 3 dB bandwidth of 1 kHz. We slowly fill the cell with N_2 and record Rydberg spectra. After each filling we empty the setup and repeat the filling again, but record groundstate spectra of the D_1 line of Rb instead. This allows to determine the Rb density by fitting a theoretical Rb groundstate spectrum to the recorded spectra in order to characterize the gas detection scheme with a second complementary method.

4. Results

Recorded current signals as function of the detuning Δ of ω_C from the Rydberg line are plotted in figure 1(b) for different ratios of Rb to N_2 . Measurements without a buffer gas were performed in [22]. Next to the main $5S_{1/2}$, $F = 3 \rightarrow 5P_{1/2}$, $F = 2 \rightarrow 32S$ transition appears a second peak emerging from atoms flying towards the propagation direction of ω_P , which are due to the Doppler effect resonant to ω_P on the $5S_{1/2}$, $F = 3 \rightarrow 5P_{1/2}$, $F = 3$ transition. Each frequency sweep has a duration of 1 s over a span of 3 GHz. The coupling light has an energy of 2.6 eV, which is 0.4 eV larger than the workfunction of bulk Rb [42]. This is the reason why all spectra show an offset, which is due to the photoelectric effect on Rb sticking to the walls of the glass cell. Comparing the three spectra it is obvious that we observe less current for lower Rb concentrations.

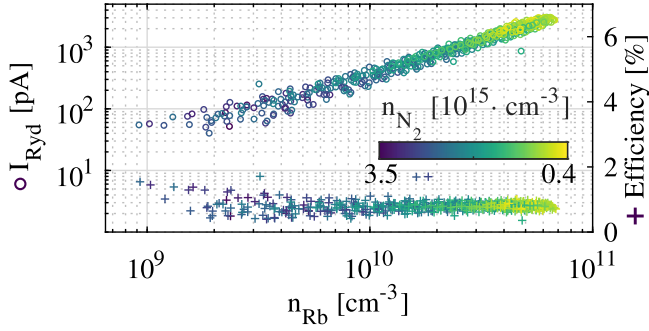


Figure 3. Amplitude of the Rydberg current spectra on the left axis and detection efficiency on the right axis as function of the ^{85}Rb density. The color code depicts the N_2 density.

The amplitude of the current signal is obtained by fitting a Lorentz function to the current signal. An exemplary measurement of the amplitude as function of the N_2 density is depicted in figure 2 together with the ^{85}Rb density. The Rb needs to diffuse through the N_2 background gas [43, 44] to the excitation region. The Rb density is therefore not uncorrelated from the N_2 density.

For small Rb densities, the optical density is too low to reliably fit a D1 line spectrum to the recorded data. This unfortunately limits the determination of the detection limit of the gas sensor to the smallest optically detectable Rb density. It nevertheless provides an upper limit of the detection limit of 500 ppb. The important point to note here is that the Rydberg-created current signal continuous further on and decreases by another order of magnitude until it finally vanishes in the noise floor of the employed amplifier.

Using these measurements as calibration, we are able to plot the measured Rydberg current as function of the ^{85}Rb density, which is shown in figure 3. The statistical spread towards low concentrations of Rb is caused by the before mentioned problems in the calibration. The small variations between the measurements are a result of the varying Rabi frequency of the coupling transition. This is not only caused by the light source itself but also by scattering at Rb condensed onto the glass walls. In order to assess the detection efficiency we theoretically calculate the expected current with equation (1). We solve the Liouville-von Neumann equation for a three level system, similar to [22] to determine the relative Rydberg population ϱ_{33} . To obtain an upper limit for the expected current, we assume the decay Γ_{ion} of the Rydberg population to be caused by ionization solely and estimate it from the width of the current signal in figure 1(b). We also do not subtract possible contributions from power or Doppler broadening. The ratio of the actually measured current to the estimated current is plotted on the right axis in figure 3. The persistence of this lower estimate of the detection efficiency over the whole range of Rb to N_2 concentrations shows that possible loss mechanisms such as charge recombination, quenching and purely radiative decay although certainly present, do not spoil the linearity of the sensing scheme.

In order to show how much better the Rydberg current detection is, compared to the optical groundstate spectroscopy, we extract the signal to noise ratio $\text{SNR} = S/N$ from the

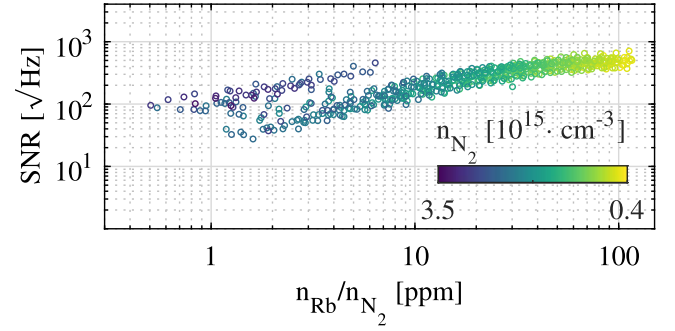


Figure 4. SNR as function of the concentration of Rb to N_2 density. The color code depicts again the N_2 density.

measurements in figure 1(b). The signal amplitude S is still given by the amplitude of the Lorentz function fitted to the Rydberg signal. N is the rms noise amplitude, extracted from the root mean square value of the spectral noise density, which we obtain from Fourier transforming the offresonant current signal. This is plotted in figure 4 as function of the concentration. The sudden step is caused by switching the gain of the employed transimpedance amplifier to avoid saturation. The smaller transimpedance gain leads to more thermal noise of the amplification circuit. Also observable is that the SNR does not increase linearly. This is because a large contribution to the noise is provided by the intrinsic shot noise of the photocurrent. This photocurrent and hence also the noise contributed to it increase as the amplitude of the Rydberg signal rises.

There are two ways to further enhance the SNR and hence also lower the detection limit. The most obvious possibility is to increase the Rabi frequency on the upper ω_C transition by increasing the laser power up to the saturation limit. In principle 35% of all ^{85}Rb atoms can be transferred to the Rydberg state [45] with sufficient laser power, e.g. in a pulsed excitation. While so far we only achieved 0.01%. The other possibility is to improve the noise properties of the sensor. One contribution is the presence of the photocurrent caused by Rb sticking to the cell walls. Even worse the overall coating with metal leads to a tiny current driven by the bias voltage U_{bias} . The bias voltage also increases the input voltage noise of the amplifier [46]. Since an external amplifier is used for this experiment a lot of noise is picked up by insufficient shielding and microphonic noise caused from slight movements of the cables. Furthermore the capacity of the long electrical leads contributes to the overall noise by converting the input voltage noise into an effective input referred current noise. This is why a major improvement of the properties of the gas sensor will be to place the transimpedance amplifier as close as possible to the source of the current, i.e. directly into the glass cell [30, 32, 47]. We think that the largest contribution to the systematic errors of our experiment is given by the gas mixture preparation. To improve the sample preparation further analysis of different materials, cell geometries and flow speeds have to be conducted.

5. Summary

The proposed detection scheme shows many advantages compared to already existing sensing technologies without apparent drawbacks. The cw excitation of Rydberg atoms is beneficial for the selectivity and resolution of the sensing scheme, since its linewidth is significantly smaller than in a pulsed excitation [30]. Like this, the sensing scheme can really benefit from the resonant n-photon excitation. Unfortunately the independent calibration of the sensor remains challenging and limits the determination of the detection limit to an upper estimate of 500 ppb with a SNR of 100 at 1 ppm. There are still some issues which were not investigated in the present realization. The dynamic range in terms of absolute amount of Rb is rather small. Also, a long term study of drift and reliability of the sensor is yet not under consideration. Furthermore an applicability on a real-life sample including excessive amounts of other very dissimilar gas components like humidity in exhaled breath still remains to be proven.

Acknowledgments

This work is supported by EU.H2020.macQsimal ID:820393.

ORCID iDs

H Kübler  <https://orcid.org/0000-0001-5110-5337>

References

- [1] Riegel J 2002 *Solid State Ion.* **152–153** 783
- [2] Yang R and Chen R 2010 *Sensors* **10** 5703
- [3] Wilson A 2013 *Sensors* **13** 2295
- [4] Li S, Simonian A and Chin B A 2010 *Electrochem. Soc. Interface* **19** 41
- [5] Buszewski B, Keszy M, Ligor T and Amann A 2007 *Biomed. Chromatogr.* **21** 553
- [6] Ishihara T and Matsubara S 1998 *J. Electroceram.* **2** 215
- [7] Wang C, Yin L, Zhang L, Xiang D and Gao R 2010 *Sensors* **10** 2088
- [8] Umar Ahmed 2009 *Metal Oxide Nanostructures and their Applications* (Valencia, CA: Amer Scientific Publishers)
- [9] Fanget S, Hentz S, Puget P, Arcamone J, Matheron M, Colinet E, Andreucci P, Duraffourg L, Myers E and Roukes M 2011 *Sensors Actuators B* **160** 804
- [10] Kim S, Lee Y-I, Choi Y-M, Lim H-R, Lim J-H, Myung N V and Choa Y-H 2015 *Nanotechnology* **26** 145503
- [11] Hodgkinson J and Tatam R P 2012 *Meas. Sci. Technol.* **24** 012004
- [12] Lewicki R, Doty J H, Curl R F, Tittel F K and Wysocki G 2009 *Proc. Natl Acad. Sci.* **106** 12587
- [13] Heinrich K, Fritsch T, Hering P and Mrtz M 2009 *Appl. Phys. B* **95** 281
- [14] Ménil F, Coillard V and Lucat C 2000 *Sensors Actuators B* **67** 1
- [15] Bakker E 2004 *Anal. Chem.* **76** 3285
- [16] Stetter J R and Li J 2008 *Chem. Rev.* **108** 352
- [17] Awad H, Khamis M M and El-Anead A 2014 *Appl. Spectrosc. Rev.* **50** 158
- [18] Glish G L and Vachet R W 2003 *Nat. Rev. Drug Discovery* **2** 140
- [19] 2005 *The PID Handbook—Theory and Applications of Direct-Reading Photoionization Detectors* (RAE Systems Inc)
- [20] Radziemski Leon J., Solarz Richard W. and Paisner Jeffrey A. 1987 *Laser spectroscopy and its applications* (New York: Marcel Dekker, Inc.)
- [21] McKeachie J R, van der Veer W E, Short L C, Garnica R M, Appel M F and Benter T 2001 *Analyst* **126** 1221
- [22] Barredo D, Kübler H, Daschner R, Löw R and Pfau T 2013 *Phys. Rev. Lett.* **110** 123002
- [23] Daschner R, Ritter R, Kübler H, Frühauf N, Kurz E, Löw R and Pfau T 2012 *Opt. Lett.* **37** 2271
- [24] Ryabtsev I I, Tretyakow D B, Beterov I I, Bezuglov N, Micullis K and Ekers A 2005 *J. Phys. B: At. Mol. Opt. Phys.* **38** 17
- [25] Glukhov I L and Ovsiannikov V D 2009 *J. Phys. B: At. Mol. Opt. Phys.* **42** 075001
- [26] Li L, Shi X, Findley G and Evans C 2009 *Chem. Phys. Lett.* **482** 50
- [27] Komatsu M, Ebata T and Mikami N 1993 *J. Chem. Phys.* **99** 9350
- [28] Ashfold M N R, Hartree W S, Salvato A V, Tutchter B and Walker A 1990 *J. Chem. Soc., Faraday Trans.* **86** 2027
- [29] Jungen C and Miescher E 1969 *Can. J. Phys.* **47** 1769
- [30] Schmidt J et al 2018 *Appl. Phys. Lett.* **113** 011113
- [31] Daschner R, Kübler H, Löw R, Bauer H, Frühauf N and Pfau T 2014 *Appl. Phys. Lett.* **105** 041107
- [32] Schmidt J, Schalberger P, Baur H, Löw R, Pfau T, Kübler H and Frühauf N 2018 *Quantum Technologies 2018* (<https://doi.org/10.1117/12.2309655>)
- [33] Djekic D, Fantner G, Behrends J, Lips K, Ortmanns M and Anders J 2017 *ESSCIRC 2017—43rd IEEE European Solid State Circuits Conf.* pp 79–82
- [34] Worden E F, Conway J G and Paisner J A 1978 *Opt. Lett.* **3** 156
- [35] Hermann J P and Wynne J J 1980 *Opt. Lett.* **5** 236
- [36] Niemax K 1985 *Appl. Phys. B* **38** 147
- [37] Rotondaro M D and Perram G P 1997 *J. Quant. Spectrosc. Radiat. Transfer* **57** 497
- [38] Hahn Y 1981 *J. Phys. B: At. Mol. Phys.* **14** 985
- [39] Petitjean L, Gounand F and Fournier P R 1984 *Phys. Rev. A* **30** 736
- [40] Thompson D C, Kammermayer E, Stoicheff B P and Weinberger E 1987 *Phys. Rev. A* **36** 2134
- [41] Safarian J and Engh T A 2012 *Metall. Mater. Trans. A* **44** 747
- [42] Hall T and Mee C 1974 *Phys. Status Solidi* **21** 109
- [43] Ishikawa K and Yabuzaki T 2000 *Phys. Rev. A* **62** 065401
- [44] Sushkov A O and Budker D 2008 *Phys. Rev. A* **77**
- [45] Huber B, Baluktsian T, Schlagmüller M, Kölle A, Kübler H, Löw R and Pfau T 2011 *Phys. Rev. Lett.* **107** 243001
- [46] Graeme J 1996 *Photodiode Amplifiers: OP AMP Solutions* (McGraw-Hill Education) Gain technology
- [47] Schmidt J, Schalberger P, Baur H, Löw R, Pfau T, Kübler H and Frühauf N 2017 *21st Int. Workshop Active-Matrix Flatpanel Displays and Devices (AM-FPD)* p 296