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Abstract

Advanced methodologies and experiments have been shown in the field of high-resolution infrared and microwave spectroscopy, suitable for the identification and concentration monitoring of small reactive molecules (molecular radicals and ions).

The methodology for spectroscopic studies of molecular ions has a unique characteristic in that it enables not only the detection and distinction of ions from neutral species but also the distinction between anions and cations. Some results of molecular ion spectroscopy related to cation ArD^+ , anion SD^- have been presented.

The formation mechanisms of HCN/HNC in extended negative glow discharge plasma were studied with the help of the frequency-magnetic field double modulation technique. The ability to distinguish the generation of HNC and HCN by ionic reactions from that from neutral reactions was used.

Important intermediates of the halogen hydrocarbon degradation processes in reactions in the atmosphere, in combustion and in combustion processes have been studied. The molecular radicals include FCO_2 , CH_2Cl and CH_2Br .

Several micromechanical elements (multilayer muscovite and multilayer graphene cantilevers with thicknesses $< 1 \mu\text{m}$) as part of an optical microphone in photoacoustic spectroscopy by using either a discretely tuneable CO_2 laser or quantum cascade (QC) lasers as the radiation source have been tested. A special photoacoustic cell was designed to compare the sensitivity of these elements to a commercial high-class condenser microphone. The responsivity to acoustic pressure was found to be two orders of magnitude higher than that of the microphone, and the cantilevers prepared from layered materials show promise as pressure-sensitive elements.

The applicability of a photoacoustic method, called cantilever-enhanced photoacoustic spectroscopy, in combination with quantum cascade lasers for biomass burning product monitoring was discussed. We found that several of the most abundant species produced by biomass burning have absorption lines within the tuning range of commercial quantum cascade lasers. The detection limits of some of these species were determined under laboratory conditions using a commercial photoacoustic unit along with quantum cascade lasers. Using these data and the spectral information available from the HITRAN database, the detection limits for several species in the tuning range of the

commercially available QC lasers were estimated, and the cross-sensitivities were evaluated.

Two mixtures of acetone/acetic acid/methanol were analysed, where both contained acetone in excess. We demonstrated that this method is suitable for measuring acetic acid with a high background of acetone. The results are of importance for medical breath analysis.

LIDAR technology has been advanced in the last four decades to become an eminent remote sensing tool, even for monitoring dense forests, topographical objects and ecological subjects.

The urban street canyon of Legerova Street is part of the north-south trunk road that passes through the centre of Prague. As many as one hundred thousand cars move through this street canyon per day, and mortality rates have increased as a result of dust, NO_x and other exhaust pollutants. The spatial distribution of pollutants (i.e., NO₂, NO, and O₃) during a day was measured by combined DIAL/SODAR techniques and spot analysers that were appropriately located near the bottom of the street canyon. The measurements were performed under different meteorological conditions (an autumn versus a summer period). A purely physical approach does not provide a true description of reality due to photochemical processes that take place in the street canyon atmosphere.

Introduction

The combustion processes and industrial processes producing toxic species (intermediates and end products) have a very large environmental impact. Characterization of these processes by their physical and chemical effects is one of the main tasks of environmental studies. Effects can be clarified by laboratory experiments or by direct monitoring. Spectroscopic methods are suitable for gas phase concentration analysis under laboratory conditions as well as for direct detection in the atmosphere.

I would like to present my professional activities related to spectroscopic detection and analysis from small to trace concentrations in gaseous media. Such activities include spectroscopic observation of unstable species arising in the gaseous environment of low-temperature plasmas (discharges, flames) and monitoring of gaseous pollutants in air locally or remotely. We must be able to monitor concentrations at

the sub-ppm level to obtain basic information about unstable species such as ions and radical molecules. At the same level, pollutants must be monitored for their harmful effects on human health.

Local observation is an indispensable complement to air quality control, and spectroscopic techniques are evolving towards increasing sensitivity and providing high selectivity, rapid response, and a range of spectral line information. The remote detection technique has great advantages in regard to global monitoring of air pollution, but with the corresponding instrument demand. I present results obtained using spectroscopic techniques in the investigation of laboratory-produced stable and unstable species (atoms, molecules, radicals, ions) in gaseous environments and the investigation of concentration levels of gaseous pollutants in the atmosphere, where photoacoustic spectroscopy and the LIght Detection And Ranging (LIDAR) method play important roles in local detection and remote sensing, respectively.

1. Spectroscopic observation of unstable species arising in the gaseous environment of low-temperature plasmas

1.1 High-resolution spectroscopy and unstable species

An important tool of these studies is high-resolution spectroscopy, with a focus on the identification and concentration monitoring of small reactive molecules (molecular radicals and ions) [1] important in low-temperature plasmas, such as fire or electric discharge plasmas, i.e. important in the processes of combustion, electric discharge and atmospheric chemistry. The effect of conventional chemicals such as halogenated hydrocarbons on atmospheric chemistry is most noticeable in the depletion of the ozone layer. A large number of combustion processes on the Earth's surface produce greenhouse gases, acid rain and the emission of hazardous pollutants into the atmosphere that we breathe.

This part of dissertation has shown advanced methodologies and experiments in the field of high-resolution infrared and microwave spectroscopy that are suitable for the identification and concentration monitoring of small reactive molecules (molecular radicals and ions). These species were generated in low-temperature plasma or chemical, photolytic and pyrolytic reactions. All the methodologies used have one thing in common, namely, the high spectral resolution, which makes it possible to monitor energy transitions in the monitored species up to the rotational level.

1.1.1 Molecular ions

1.1.1.1 Spectroscopic analysis as a means of verification

The methodology for spectroscopic studies of molecular ions presented in this work has a unique characteristics: the detection and distinction of ions from neutral species, also the distinction between anions and cations. I have presented some results of molecular ion spectroscopy related to cation ArD^+ [2, 3], anion SD^- [4, 5]. The SD^- negative ion was detected and spectroscopically identified as the first negative ion to be observed at the rotational level in the Czech Republic. The concept of isotopically invariant parameters describing the spectroscopic features of a molecule seems to be a very efficient tool. In our studies, we applied calculation of isotopically invariant Dunham parameters to a negative ion - the hydrogen sulfide (SH^-) anion. These spectroscopic analyses represent highly effective means of verifying and identifying observed unstable species.

1.1.1.2 Branching ratio of the dissociative recombination of HCNH^+

The formation mechanisms of HCN/HNC in extended negative glow discharge plasma were studied [6-8] with the help of the frequency–magnetic field double modulation technique. The ability to distinguish the generation of HNC and HCN by ionic reactions from that from neutral reactions was used. A substantial amount of HCN was produced through neutral–neutral reactions other than the dissociative recombination of HCNH^+ . Therefore, measurements at liquid nitrogen temperature, preferably even at lower temperatures, are truly essential. At liquid nitrogen temperature, the observed HCN signal is very likely to be predominantly produced by the dissociative recombination reaction. However, the possibility of a contribution from neutral reaction channels cannot be eliminated completely. The branching ratio of the dissociative recombination leading to HCN and HNC production is derived from the abundance ratio by examining the temperature dependences of the HCN and HNC line signal intensities, as well as those of HCNH^+ . The subsequently obtained branching ratio is 3 with an estimated uncertainty of 20% for the normal species and is 1.5 for the deuterated species. This might be another reason for the larger $[\text{HCN}]/[\text{HNC}]$ ratio. The experimental value of $[\text{DCN}]/[\text{DNC}]$ agrees with the theoretical values. This result is more reasonable because deuterated species are less prone to isomerization.

1.1.2 Halogenated radicals

1.1.2.1 MW and IR spectroscopy of molecular radicals

In this part of the work, I concentrated on halogen radicals, which are among the important intermediates of the halogen hydrocarbon degradation processes in reactions in the atmosphere, in combustion and in combustion processes. Most of these intermediates, especially those of a radical nature, have not yet been identified spectroscopically and therefore cannot be easily monitored. In this dissertation, I have presented some of our significant results in the field of spectroscopic detection and identification of molecular radicals. The first spectroscopically unambiguous identification of high-resolution molecular radicals, i.e., identification at the rotational level, is one of the main results. The molecular radicals include FCO₂ [9-13], CH₂Cl [14] and CH₂Br [15, 16]. For the FCO₂ and CH₂Br radicals, the first spectroscopic identification at this level of resolution was presented.

1.1.2.2 FCO₂ fluoroformyloxy radical

The FCO₂ fluoroformyloxy radical can play an important role in atmospheric chemistry. Degradation of halogenated hydrocarbons such as hydrochlorofluorocarbons (HCFCs) leads to cleavage into fragments of the halogenated methyl derivative type, CX₃ (X = Cl or F).

The rotational spectrum of the FCO₂ radical in the gas phase was detected, rotational and centrifugal-distortion constants were experimentally determined, and the values obtained were in good agreement with *ab initio* calculations.

Direct measurements have shown that the FC(O)O* radical survives in a collision-dominant environment for at least several milliseconds [17]. This is one reason why the fluoroformyloxy radical FCO₂* can play an important role in atmospheric chemistry.

All lines were fitted with an effective Hamiltonian [18], which involved spin-spin and spin-rotation interactions together with the corresponding distortion operators. A CALPGM fitting program [19] was used to derive spectroscopic constants.

1.1.2.3 Molecular radicals CH₂Br and CH₂Cl

The concentration of bromine in the stratosphere is much less than that of chlorine. However, several studies have demonstrated the far greater destructive capacity of bromine to stratospheric ozone compared

to chlorine. Garcia and Solomon reported the effectiveness of this destruction to be 100 times greater for bromine [20].

The most important sources of bromine in the atmosphere include methyl bromide CH_3Br . Methyl bromide is released from both anthropogenic and natural sources: it is used in pesticides or as an extinguishing agent but is also released from the oceans (degradation of algae and phytoplankton).

The rotational spectrum of the CH_2Br radical was fully analysed, and the rotational constants for both isotopomers of this radical were accurately determined.

The effective structure derived from our experimental results and the CH_2Br electronic structure derived from the fine and hyperfine splitting constants agree well with *ab initio* calculations. The resulting constants and data obtained in the final analysis phase are summarized in [15, 16].

I want to mention the results of the measurement of the CH_2Cl radical, which actually served as an optimization element in the detection of the CH_2Br radical. The molecular constants published in ref. [21] were used for prediction.

In complex systems such as flame plasma, electric discharge, and the earth's atmosphere, a number of analytical tools are needed to understand the ongoing physico-chemical processes. I have outlined how to identify the spectroscopic characteristics of some reactive molecules that are important in terms of atmospheric chemistry and combustion processes through laboratory studies.

2. Monitoring of gaseous pollutants in air

Air pollution control and the sustainability of a healthy environment are key to the sustainability and improvement of the health standards of the population of Europe and the world. Many people today are exposed to a wide range of different pollutants from combustion processes or many chemicals that strongly affect their health due to the acute toxicity and long-term effects, such as asthma, allergies or cancer. Research on new sensing technologies for controlling and monitoring air pollution is increasingly gaining importance [22].

Generally, one component to multicomponent local gas analyses are performed by chromatography in conjunction with mass spectrometry. These techniques are characterized by high sensitivity and selectivity but by a long response time (minutes) determined by

the chromatographic separation time. This response time prohibits application of these techniques in real time and for continuous monitoring of gases. In contrast, IR laser spectroscopy allows highly selective and rapid detection of most gases and vapours that exhibit a strong fundamental absorption associated with molecular vibrations in the IR region of $\lambda = 3\text{-}20\ \mu\text{m}$ [23-28].

2.1 Absorption spectroscopy

FTIR spectra [29] of several compounds that were suggested as markers in breath analysis can be used as an example of input data for multicomponent analysis (e.g. Fig. 1). The comparison shows some promising regions for performing multicomponent analysis, particularly the regions of acetic acid COH deformation, the CCO valence band at approximately $1294\ \text{cm}^{-1}$ and the OH valence band at approximately $3581\ \text{cm}^{-1}$, where acetone and methanol show low absorption [23].

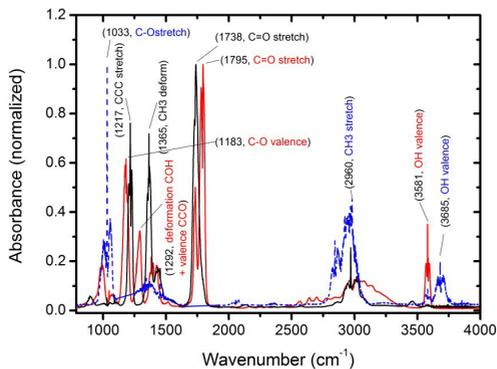


Fig. 1: Example of FTIR spectra of acetic acid (red line), acetone (black line) and methanol (blue line).

The recent development of laser sources for the mid-IR (MIR) region has brought about quantum cascade lasers (QCLs), which have initiated a new reason for the development of laser gas sensors. By selecting materials of the active region and electron injectors, QCLs in a broad spectral range of the MIR region can be prepared [27, 30-32].

2.1.1 Laser photoacoustic spectroscopy

Photoacoustic detection in connection with a laser radiation source is an effective tool for gas, liquid and solid phase investigations. The greatest strength of a laser-induced photoacoustic phenomenon lies in the simplicity based on the conversion of absorbed energy of laser photons to kinetic energy to thermal energy that will manifest itself in a change in pressure.

The production of a photoacoustic signal can be generally caused by many processes from electrostriction with a polarizable sample to thermal expansion with heat deposition through photochemistry and molecular dissociation, bubble formation and breakdown of the sample. In this order, the efficiency of photoacoustic signal generation, i.e., the ratio of generated acoustic energy to absorbed light energy, is increasing. For the mechanisms of electrostriction and thermal expansion, the level of this efficiency is 10^{-12} to 10^{-8} ; for the mechanisms of breakdown, this efficiency can even reach 30%.

2.1.2 Trace detection of gases and vapours

The photoacoustic phenomenon can be formally described by the molecular absorption of electromagnetic radiation and the subsequent generation of acoustic waves in a cell, which is described by a nonhomogeneous wave equation as a function of generated kinetic energy [33].

The primarily high sensitivity of photoacoustic detection in the IR region was achieved by using high-power gas lasers in the MIR region, i.e., especially CO and CO₂ lasers, e.g., [26, 28, 34-36]. The emissions of these lasers spectrally correspond to strong vibrational transitions of the ground states of many molecules. These spectral resonances together with the laser wattages enabled detection limits for photoacoustic detection at the ppbv level [37, 38].

By using diode lasers in the NIR region, we lose the advantage of detection at strong fundamental vibrational transitions of molecules. The last great development in the area of solid-state tunable lasers, however, enabled the return to this spectral region: the development of optical parametric oscillators (OPOs) on the basis of periodically poled lithium niobate (PPLN) [39-42] and quantum cascade (QC) diode lasers

[43, 44], with which photoacoustic systems have been implemented for trace analytics of molecules, such as formaldehyde, CO₂, butyl alcohol, NO, and hexamethyldisilazane [45, 46]. The detection limits achieved by these systems are at the sub-ppb level.

New detection techniques for photoacoustic spectroscopy have been developed. One of them is the use of quartz tuning forks (QTFs), which were originally used as chemical sensors [47] and then applied in photoacoustic spectroscopy [48]. Kosterev et al. developed the technique of quartz-enhanced photoacoustic spectroscopy (QEPAS) with high sensitivity on the basis of QTFs as photoacoustic sensors [49]. QEPAS was demonstrated in the near IR region using wavelength modulation to suppress the background and obtain high sensitivity.

Another developed detection technique for photoacoustic spectroscopy is cantilever-enhanced photoacoustic detection [50]. The best sensitivities achieved at present in photoacoustic detection were obtained by using the acoustic resonance of a photoacoustic cell and are at the level of 10^{-8} - 10^{-9} cm⁻¹W/ $\sqrt{\text{Hz}}$ (normalized noise equivalent absorption (NNEA) coefficient) [49, 51, 52]. In cantilever-enhanced photoacoustic detection, a micromachined silicon cantilever is used instead of a microphone. Shifts of this cantilever due to changes in pressure are interferometrically measured by a laser Michelson interferometer (which produces interference patterns by splitting a beam of light into two paths, bouncing the beams back and recombining them; the different paths then create alternating interference fringes on a back detector).

2.1.3 Conversion of optical energy to thermal energy

The conversion of optical energy to thermal energy depends on some physical properties of the sample, namely, not only the absorbing part of the sample but also on the properties of a buffering gas. For these reasons, photoacoustic spectroscopy is not an absolute method and requires calibration. The molecular relaxation of excited rovibrational states for sample heating is a key step towards photoacoustic signal generation. In many cases, this effect can be considered to be immediate because it is much faster than the time dimension of laser modulation. However, for some mixtures of gases, this effect is much slower, and the corresponding long relaxation time may heavily affect photoacoustic signal

generation [53, 54].

2.1.4 Microlevers for optical microphones

One of the objectives of these studies is based on micromechanical sensing elements in the frame of new sensing technologies [25]. A cantilever-type pressure sensor has been proposed instead of the microphones used in PAS to achieve optimal sensitivity [50, 55-58]. The main benefits of the cantilever are a very low spring constant and an extremely wide dynamical range of the cantilever movement. The spring constant can be 2 or 3 orders of magnitude smaller than that of the membrane of a condenser microphone, and the movement of the cantilever can be tens of micrometres without any nonlinear or restricting effects. A noncontact (deflection, interferometry) measurement of the cantilever end movement is required to avoid damping due to the probe and to maintain the wide dynamic range. Graphene or mica sheets have outstanding electromechanical properties and impressive sensitivity as mass detectors. Their mechanical properties offer utilization as micro/nanolevers. These levers could work as extremely sensitive pressure sensors or mass detectors. Realizing such types of sensing devices for chemical analysis is an important challenge [59].

A cantilever beam is one of the simplest mechanical structures (Fig. 2). If a force F is applied at the free end perpendicular to the beam, then the deflection z of the cantilever is, for a material with given Young's modulus.

In previous studies (to improve the physical modelling of urban air pollution), we developed and employed laser photoacoustic spectrometry [60-62]. The aim of this work was to design and fabricate several sensing elements of the cantilever type and to test and characterize their mechanical properties with the help of the PAS method [63]. Transducers of different materials (silicon, carbon, mica) have been employed for the design of new gas sensing elements. Fig. 3 shows the general

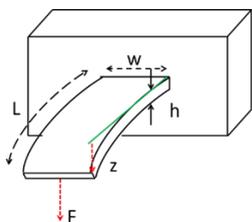


Fig. 2: Schematic of the operation principle of a cantilever.

experimental scheme for testing of sensing elements and for any PAS measurements.

Such a system is suitable for the measurement of trace gas concentrations of many species. We determined the sensitivity of the PAS system with an optical cantilever microphone in a standardized way as the NNEA coefficient. From known QC laser and absorption parameters, the detection limits for any molecule can be estimated. An example of such an estimate is shown in Fig. 4 (QC series lasers from Thorlabs, USA and *sbcw* series from Alpes Lasers, Switzerland). Species measured in our laboratory are red coloured [24].

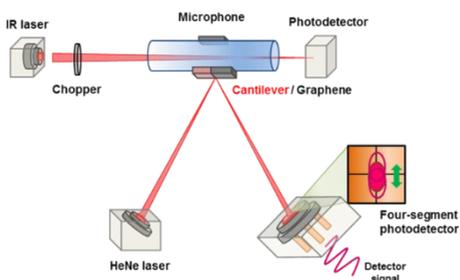


Fig. 3: Experimental scheme for testing of sensing elements and for PAS measurements.

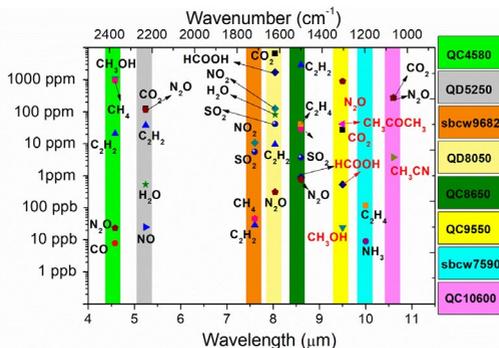


Fig. 4: Estimated detection limits of selected molecules.

2.2 Local monitoring - indispensable accessories for air quality control

2.2.1 Main tools – lasers and QCLs

Sensors based on tunable diode laser absorption spectroscopy (TDLAS) are potential candidates for the measurement of trace concentrations of many species [64]. TDLAS is a well-established spectroscopic method. Its main advantages are high sensitivity, fast response, simplicity of design and operation, nonintrusive measurement and low cost of operation. The measured narrow absorption lines (i.e., intensity and spectral position) act as a fingerprint of a given species. Trace amounts of gases can be measured down to the ppm level in the NIR region with weak overtone and combinational bands and down to ppb levels in the MIR region, for which QCLs with power on the order of tens of milliwatts are available and where many species show strongly absorbing fundamental vibrational bands [65].

We determined the detection limits and NNEA (Noise Normalized Equivalent Absorption coefficient) values for several other gases absorbing within the range of the QD9550CM1 (all but acetonitrile) and QD10600CM1AS (acetonitrile) lasers [24].

The detection limits were determined at the strongest lines within the tuning range of the laser diodes. Among these species, acetonitrile is of special importance, as it was suggested as a unique biomass burning tracer with a long lifetime in the atmosphere (~900 days) [66].

The sensitivity of this method depends on the absorption coefficient of the detected molecule, the laser wavelength, the laser intensity, the

sensitivity of the detector to acoustic pressure and the arrangement of the photoacoustic cell. The last topic was the subject of a literature review [67]. Kauppinen et al. [50] showed that the sensitivity of conventional (i.e., electret and condenser) microphones can be surpassed by using an optical microphone, where the movement of a pressure sensitive element, i.e., a silicon cantilever, is monitored by a laser beam that is reflected from that element onto a position sensitive detector.

We envisioned that the low-dimensional materials prepared from layered precursors could have suitable mechanical properties, such as pressure sensitive elements [63]. For photoacoustic detection, a micromechanical detector with cantilevers prepared from layered materials, i.e., highly ordered pyrolytic graphite (HOPG) and muscovite (mica), was used. We compare three different elements: a mica circular cantilever, a mica rectangular cantilever, and a multilayer graphene (MLG) cantilever of low thickness (as low as 100 nm).

2.2.2 Experimental details – arrangement and lever systems

A general scheme of the experimental setup is depicted in Fig. 3. A discretely tunable CO₂ laser (Edinburgh Instruments WL-8-GT, Livingstone, Scotland) emitting in a spectral range of 9-11 μm or QC lasers (see Fig. 4) were used as an excitation source. Details can be found elsewhere [23, 24, 26, 63].

2.2.3 Sensitivity of the tested elements and multicomponent analysis

The sensitivity of the elements was determined as the detection limit for methanol vapours. This limit was determined by the method described in [68] from the calibration curve.

The resulting calibration curves are shown in Fig. 5. The best sensitivity (in terms of the slope of the calibration lines) is achieved using the rectangular mica cantilever [23].

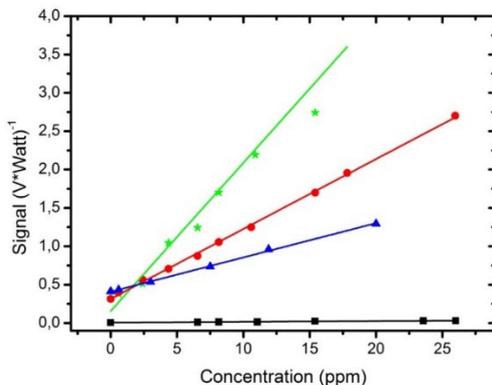


Fig. 5: Calibration curves of the microphone (black squares, 166 Hz), MLG cantilever (blue triangles, 252 Hz), circular mica cantilever (red circles, 275 Hz) and rectangular mica cantilever (green stars, 581 Hz). Tested gas – methanol. Frequencies in brackets give the modulation (chopper) frequency.

The circular mica cantilever was chosen as the photoacoustic sensor for performing these analyses. The detection limits for individual molecules were determined for this cantilever at the lines with the best sensitivity [23].

For the multicomponent analysis, five CO_2 laser lines were selected (9.24, 9.5, 9.58, 10.2 and 10.24 μm). Multicomponent analysis was performed for the ~10:1:1 mixture of acetone:acetic acid:methanol (Table I. I) [23].

Table I. Results of multicomponent analysis. The concentrations of individual compounds are in ppm.

Compound	I		II	
	Prepared	Calculated	Prepared	Calculated
Acetone	65	70	3950	4200
Acetic acid	6.2	6.0	10.7	2.6
Methanol	6.5	3.4	10.6	12.5

The calculated results are in good agreement with the actual concentrations for acetone and acetic acid (errors of 7% and 3%, respectively) but somewhat surprisingly (considering the spectra) are almost 50% different for methanol.

Considering the photoacoustic signal of acetic acid and acetone at various CO₂ laser lines, the measured PA signal at 10.24 μm (per watt and ppm), which is directly proportional to the absorption coefficient, is almost 500 times higher for acetic acid than for acetone. We can assume that one part acetic acid can be detected in 500 parts acetone. This is important for breath analysis because the concentration of acetone in the breath of a healthy person (in the ppm range) can be more than 25 x higher than that of acetic acid (40–80 ppb) [69, 70].

We also tested a mixture with a significantly higher concentration of acetone (almost 400 x higher than that of acetic acid and methanol; see Table I. II) [23]. Here, the signal of the mixture was dominated by the acetone signal. The calculated concentrations for acetone, acetic acid and methanol differed by 7%, 76% and ~20%, respectively, from the actual concentrations. The multicomponent analysis of the mixture of acetic acid, acetone and methanol was performed with the photoacoustic setup equipped with the circular mica cantilever using five selected CO₂ laser lines. We demonstrated that this method is suitable for measuring acetic acid under a high background of acetone. The results are of importance for medical breath analysis.

3. Remote Sensing

3.1 LIDAR as a laser remote sensing tool for atmospheric measurements

The results of a large number of interdisciplinary investigations

clearly proved the impact of anthropogenic atmospheric pollutants on humans and other parts of the environment [71]. To cover a local, regional, and global scale, input information must be available through effective advanced techniques; remote sensing methods belong to this category of techniques.

The remote sensing detection of atmospheric pollutants [72] is based on the same principles as “classical” optical methods of chemical analysis; that is, a piece of information about the chemical constitution of the atmosphere is encoded in both the results and the properties of the spectroscopic interactions between the radiation (as a probe) and atmospheric matter. These interactions compound to decrease the radiation intensity when passing through a long distance in the atmosphere (10^1 m – 10^1 km), from the source to the detector.

Generally, remote sensing techniques can be performed in passive mode with natural radiation sources, such as the sun (e.g., correlation spectrometry), or in active mode using artificial radiation sources, such as lamps or lasers (e.g., differential optical absorption spectroscopy and tuneable diode laser absorption spectroscopy). In all cases, the transparency condition must be fulfilled [73].

In principle, two main groups of optical methods are applicable for active remote sensing of the atmosphere: long-path absorption techniques and LIDAR [74-78]. The first group of methods uses continuous sources of radiation and thus enables the assessment of only the average concentration of a pollutant along the whole radiation trajectory. The advantage of LIDAR techniques is their ability to provide particular information about the distribution of pollutants along the beam trajectory. The use of pulse laser sources permits this feature.

As the transmitted laser energy passes through the atmosphere, gas molecules and particles or droplets cause scattering. A small fraction of this energy is backscattered in the direction of the LIDAR system and is available for detection. The scattering of energy in directions other than the direction of propagation or absorption by the gases and particles reduces the intensity of the beam, which is said to be attenuated. Such attenuation applies to both paths (to and from) the distant backscattering region.

There are several scattering/absorption mechanisms that occur when the laser energy interacts with the atmosphere. The predominant type of scattering is quasi-elastic scattering from

aerosols (Mie scattering) or molecules (Rayleigh scattering). Another form of atmospheric elastic scattering is resonance fluorescence. Inelastic scattering includes Raman scattering and non-resonance fluorescence. These scattering processes, sometimes in combination with molecular absorption, form the basis for various types of LIDAR remote sensing techniques. The most well-known techniques are Differential Absorption LIDAR (DIAL) and Differential Absorption Scattering Energy (DASE).

3.2 LIDAR equation

Gas molecules exhibit very irregular wavelength dependencies. The quantum nature of the absorption dictates that the molecule can move to only one of the discrete higher energy levels. Therefore, the absorption coefficients are sharply peaked functions of frequency in the form of a series of spectral lines. These lines have finite spectral widths resulting from various line-broadening effects. The transition from one quantized bound energy state to another can be rotational, vibrational or electronic, corresponding to a specific wavelength region [79].

The transmitted laser beam becomes scattered in all directions at all altitudes; the backscattered echoes are received by the telescope, and their intensities are measured. The telescope field of view is maintained to be larger than the beam divergence to completely accommodate the beam at all altitudes. For the monostatic configuration in which both the transmitter and receiver are co-located, the instantaneous intensity $I(r, \lambda)$ of the received radiation of wavelength λ can be expressed as a function of the range r between its scattering point and the received location by means of the so-called LIDAR equation; see, e.g., [80], representing an analogy to the radar equation.

The attenuation of radiation caused by the selective absorption of atmospheric constituents is employed by DIAL techniques, which are applicable for the remote sensing of typical air pollutants. In this technique, the laser transmitter emits short laser pulses of two wavelengths, λ_{on} (commonly referred to as an online wavelength) and λ_{off} (termed an offline wavelength), which are usually chosen to be inside and outside the absorption band of the pollutant of interest, respectively.

The process for calculating the concentration $C(r)$ from the recorded waveforms of intensities $I(r, \lambda_{\text{on}})$ and $I(r, \lambda_{\text{off}})$ of the received radiation is schematically diagrammed in Fig. 6.

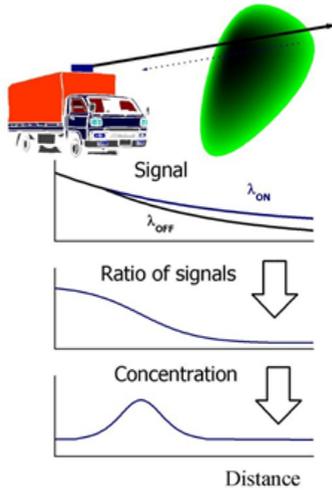


Fig. 6: Principle of a DIAL-type LIDAR system in the monostatic configuration.

3.3 Traffic-related airborne pollutants in urban street canyons

An urgent topic in urban air-quality studies is the dispersion of toxic pollutants within urban street canyons [81] - streets that are lined with buildings on both sides. Within these domains, large quantities of emissions are released, mainly through motor vehicle exhaust, and are then trapped and concentrated within the canyon walls. Urban street canyons also contain many people inside the buildings and/or in cars, potentially making these areas high-risk health zones [82, 83]. Gathering information on pollutant distribution is therefore a crucial starting point for planning effective measures to improve the air quality and optimize urban design.

Monitoring the air pollution distribution requires a setup containing a large and dense network of sample spots and/or the use of remote sensing techniques. The advantage of remote sensing techniques is their ability to provide information about the distribution of pollutants along with their radiation trajectories. To monitor the distribution of gaseous pollutants, long-path absorption

spectroscopy [84], Raman spectroscopy and DIAL are typically employed [85].

In our studies, we used remote sensing DIAL measurements and spot analyser monitoring to obtain 2D and 3D profile measurements of NO₂ and O₃. DIAL is a laser remote sensing technique that belongs to a group of LIDAR techniques [73, 74, 76, 77, 86]. Spot measurements can be used to add further information related to the concentrations of analytes in places that are inaccessible to DIAL and related to other pollutants such as NO, CO, and SO₂. The measurements were performed in a real urban street canyon, Legerova Street, with an extensive amount of traffic. This street is a part of a north-south trunk road that passes through the centre of Prague and remains an unresolved environmental issue for the capital of the Czech Republic.

The concentration of dust particles was found to be two orders of magnitude higher than the allowed level. As many as one hundred thousand cars move through Legerova Street per day, and mortality rate increases have been observed due to dust, NO_x and other exhaust pollutants. People living on this street have a drastically higher risk of developing lung cancer (growth 52%) and cardiovascular disease (growth 44%) [87, 88]. The experimental results from our Legerova Street measurements were compared using a model.

3.3.1 LIDAR measurements in the real street canyon

The DIAL/sonic detection and ranging (SODAR) system was located approximately 650 m from the traffic entry point of the street canyon. This distance was ideal with respect to the geometric compression of the measuring system and was one of the major factors influencing the correct evaluation of the measured data. The monitored street canyon area was 700 m long. The vertical distribution was mapped repeatedly by means of two-dimensional vertical scans above the street. The scans through the atmosphere were performed in such a manner that they followed the diagonal of the street canyon's ground plan.

3.3.2 Chemical reactions that occur in a street canyon

The mixture of nitrogen oxides emitted from automobiles mainly consists of NO that is partially oxidized by atmospheric oxygen to NO₂ in hot vehicle exhausts. Due to the relatively short distances in

the frame of a street canyon, only the fastest chemical reactions can have a significant influence on the transformation processes street canyon air. Most of the pollutants emitted from traffic can be considered inert components. However, nitrogen oxide gases are extremely important not only for the chemical transformations that occur inside street canyons but also for the impact of traffic pollution on human health. Regarding health effects, NO is considered to be harmless; in contrast, NO₂ can have severe adverse health effects in humans. A competitive reaction of NO with ozone is dominant in the atmosphere under common atmospheric conditions. This reaction is an order of magnitude faster than NO oxidation by molecular oxygen [89]. This suggests that the reaction between oxygen radicals and molecular oxygen is very fast. Consequently, for all practical purposes, the whole complex reaction system of NO, NO₂, and O₃ can be restricted to the production of NO₂ as a product of the reaction between NO and ozone and the photodissociation of NO₂, which leads to the reproduction of NO and O₃. The time scales of these reactions are on the order of tens of seconds and are thus comparable to the residence times of the pollutants in a street canyon; the residence time of a pollutant controls the exchange rate between the street and the background air.

3.3.3 Street canyon modelling

We assume that a street canyon is divided into layers with homogeneous concentrations. The concentration in the lowest layer is determined by vehicle emissions. The concentration in the highest layer is also determined exogenously through various factors, including environmental influences. Diffusion processes take place between adjacent layers. The chemical reactions that occur between these layers can be described by the Berkowicz model [90-92].

3.3.4 DIAL and spot measurements of pollutants

The NO₂ concentration measurements during the autumn were determined primarily using concentrations of NO and O₃ with a small contribution of NO₂ photodissociation because the level of solar radiation was small (approximately 50 W/m²); therefore, the rate constant was low. The vertical and temporal distributions of NO₂ depended mainly on the traffic, i.e., the number of cars that produced NO.

The vertical distribution of NO₂ in the autumn period mainly exhibited diffusion or homogeneous characteristics. The nondiffuse

distribution of NO_2 concentrations was related to the transport of pollutants within the street canyon and to the background ozone concentration. The small amount of traffic resulted in a low production of NO (and subsequently NO_2) during the night. Ozone is located in the upper layers of the atmosphere above the canyon street due to its relatively long lifetime [93] and is not reduced by a reaction with NO at night. Thus, O_3 molecules descend to the bottom of the street canyon. Then, in the morning hours, the O_3 reacts with the NO molecules produced by cars to form an inverse nondiffuse vertical concentration distribution of NO_2 .

The vertical profiles of O_3 concentrations were significantly influenced by the reaction of NO with O_3 . A strong reduction in O_3 concentrations at altitudes up to 40-80 m was observed from the early morning hours through the morning hours. The amount of traffic decreased over the lunch hours, and the production of NO molecules subsequently decreased. Ozone molecules, in comparison to the much lighter nitrogen molecules, dropped to the bottom of the street canyon. Based on the O_3 distribution measurements, we clearly interpreted that ozone molecules accumulated in the upper layers above the street canyon in the summer months. If such molecules were not reduced by NO molecules, they penetrated into the lower layers of the street canyon.

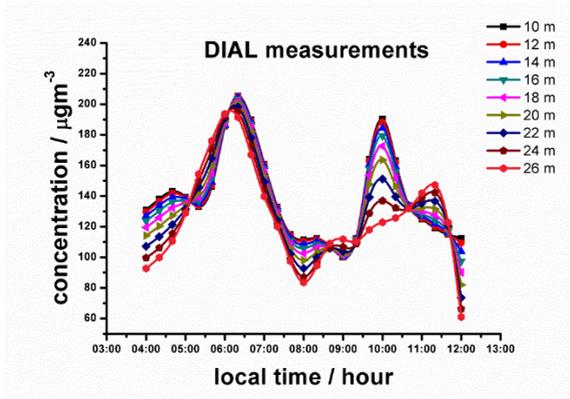
In the morning hours, the ozone concentration reached considerably higher values only above an altitude of approximately 80 m relative to the ground of the street canyon. A reason for this observation may be the NO reaction with the ozone that was consumed during the conversion of NO to NO_2 . Thus, with an increase in the distance from the ground, the NO_2 concentration did not decrease as predicted by models that neglected the presence of possible chemical reactions in the investigated system.

3.3.5 Comparison of the experimental data with the model predictions

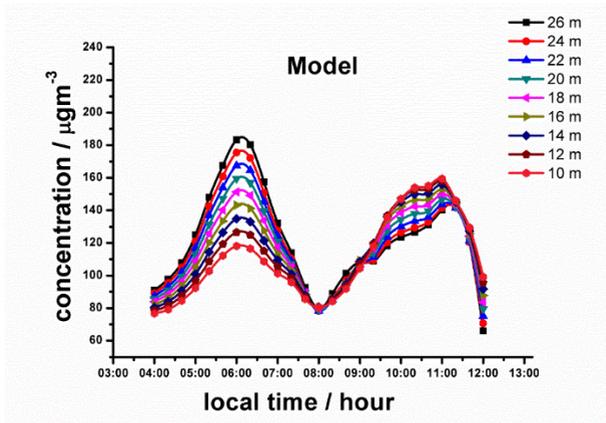
The considerable differences between the models and the experimental measurements obtained in July can be interpreted based on the reactions of the NO – NO_2 – O_3 chemical system in the atmosphere [94, 95]. We considered basic chemical reactions in a street canyon in periods with low and high levels of solar radiation and then compared the experimental data to a model. Concentration changes at different times were induced by both chemical and physical processes, such as air

exchange with the surroundings and direct emissions from cars. Two large increasing areas of NO_2 concentration dominated in the experimental data and in the model (Fig. 7). The first of the two peaks corresponded to the beginning of increased car traffic at approximately LT 06:00 and thus represented the beginning of the production of the NO that reacted with the ozone that had accumulated overnight. The second of the two peaks corresponded to the growth in the ozone concentration levels due to the influence of solar radiation that penetrated the atmosphere in the street canyon space at approximately LT 10:00; combined with the rush hour traffic, these factors caused an increase in NO_2 concentrations. CO molecules were considered inert, so their concentrations varied only due to physical processes. Measurements showed that the concentration of CO was significantly correlated to the concentration of NO_x . It follows that the NO_x concentration was also likely to change only based on the same physical effects. The sum $[\text{NO}_2] + [\text{O}_3]$, i.e., the number of potential oxygen radicals hidden in molecules, was found to grow slowly. In general, there are two potential sources of "hidden" oxygen radicals (O^*): the direct emissions of cars and the surrounding environment. If these hidden radicals were caused by the direct emissions of cars, then the concentration of hidden O^* should have been correlated with the concentration of CO . The main source of CO was only the direct emissions of cars (as indicated in the real-time composition of vehicle emissions). It is therefore likely that the main source of growth was the hidden O^* from the surrounding environment. Using these considerations for our model, we found that the model and experimental data were in good agreement, albeit with some discrepancies (see Fig. 7).

It cannot be presumed that the chemical conversions in question could have taken place in the canyon only in the summer period. The November measurements, however, did not demonstrate an apparent photochemical ozone generation effect inside the canyon, as was observed in July. The intensity of the



a)



b)

Fig. 7: Experimentally obtained NO₂ concentrations a) together with the modelling results and b) for the time development of the vertical distribution of NO₂ in the canyon of Legerova Street, as measured in July.

solar irradiation striking the bottom of the street canyon remained a limiting factor. In November, the particular NO, NO₂ and O₃

concentration ratios were insufficient for initiating a significant shift in the actual photochemical steady state to form higher ozone concentrations at the bottom of the canyon. Then, higher NO_2 concentrations at altitudes above 50 m relative to the canyon bottom can be explained based on the NO conversion to NO_2 , but only in an environment with higher ozone concentrations than the troposphere background.

It is obvious that a real street canyon represents a very complicated system. This complexity is the reason why a model approach (Fig. 7b) to the solution of such a comprehensive problem, much like the consideration of pollutant dispersion in the system, remains necessary. However, the presented results of DIAL monitoring should be extended to model studies with some basic simulations of the chemical reactions in the system to enable such model approaches to mimic reality as precisely as possible.

4. CONCLUSIONS

4.1 Laboratory measurements of unstable species

One part of this dissertation has shown advanced methodologies and experiments in the field of high-resolution infrared and microwave spectroscopy that are suitable for the identification and concentration monitoring of small reactive molecules (molecular radicals and ions). These species were generated in low-temperature plasma or chemical, photolytic and pyrolytic reactions. All the methodologies used have one thing in common, namely, the high spectral resolution, which makes it possible to monitor energy transitions in the monitored species up to the rotational level. This means that these methodologies are highly selective and the subsequent spectroscopic identification is unambiguous.

The methodology for spectroscopic studies of molecular ions presented in this work has a unique characteristic in that it enables not only the detection and distinction of ions from neutral species but also the distinction between anions and cations. I have presented some results of molecular ion spectroscopy related to cation ArD^+ [2, 3], anion SD^- [4, 5]. The SD^- negative ion was detected and spectroscopically identified as the first negative ion to be observed at the rotational level in the Czech Republic. The formation mechanisms of HCN/HNC in extended negative glow discharge plasma were studied [6-8] with the help of the frequency-magnetic field double modulation technique. The ability to

distinguish the generation of HNC and HCN by ionic reactions from that from neutral reactions was used. A substantial amount of HCN was produced through neutral–neutral reactions other than the dissociative recombination of HCNH^+ .

I have presented some of our significant results in the field of spectroscopic detection and identification of molecular radicals. The first spectroscopically unambiguous identification of high-resolution molecular radicals, i.e., identification at the rotational level, is one of the main results. The molecular radicals include FCO_2 [9-13], CH_2Cl [14] and CH_2Br [15, 16]. For the FCO_2 and CH_2Br radicals, the first spectroscopic identification at this level of resolution was presented.

In complex systems such as flame plasma, electric discharge, and the earth's atmosphere, a number of analytical tools are needed to understand the ongoing physico-chemical processes. I have outlined how to identify the spectroscopic characteristics of some reactive molecules that are important in terms of atmospheric chemistry and combustion processes through laboratory studies.

4.2 Monitoring of air pollutants

We tested several micromechanical elements (multilayer muscovite and multilayer graphene cantilevers with thicknesses $< 1 \mu\text{m}$) as part of an optical microphone in photoacoustic spectroscopy by using either a discretely tuneable CO_2 laser or quantum cascade (QC) lasers as the radiation source [25, 26, 63]. The responsivity to acoustic pressure was found to be two orders of magnitude higher than that of the microphone, and the cantilevers prepared from layered materials show promise as pressure-sensitive elements.

Lowering the noise and improving the long-term stability of the signal was a crucial task for improving the sensitivity and stability of the system [28].

The applicability of a photoacoustic method with a special micromechanical lever, called cantilever-enhanced photoacoustic spectroscopy, in combination with quantum cascade lasers for biomass burning product monitoring was discussed [24]. We found that several of the most abundant species produced by biomass burning have absorption lines within the tuning range of commercial quantum cascade lasers. The detection limits of some of these species were determined under laboratory conditions using a commercial photoacoustic unit along with quantum cascade lasers. Using these data and the spectral

information available from the HITRAN database, the detection limits for several species in the tuning range of the commercially available QC lasers were estimated, and the cross-sensitivities were evaluated.

The multicomponent analysis of an acetic acid, acetone and methanol mixture was performed [23] with a photoacoustic setup. Two mixtures of acetone/acetic acid/methanol were analysed, where both contained acetone in excess. We demonstrated that this method is suitable for measuring acetic acid with a high background of acetone. The results are of importance for medical breath analysis.

4.3 Remote sensing

LIDAR technology has been advanced in the last four decades to become an eminent remote sensing tool, even for monitoring dense forests, topographical objects and ecological subjects. The basic advantage of using LIDAR remote sensing for such applications is that it provides information on the three-dimensional structures that characterize the vegetation heights, vertical distributions of canopy materials, crown volumes, subcanopy topographies, biomass, vertical foliage diversity and multiple layers, heights to the live crowns, large tree densities, leaf area indexes, physiographic or life form diversities, etc.

The urban street canyon of Legerova Street is part of the north-south trunk road that passes through the centre of Prague and remains an unresolved environmental issue for the capital of the Czech Republic. As many as one hundred thousand cars move through this street canyon per day, and mortality rates have increased as a result of dust, NO_x and other exhaust pollutants. The spatial distribution of pollutants (i.e., NO_2 , NO , and O_3) during a day was measured by combined DIAL/SODAR techniques and spot analysers that were appropriately located near the bottom of the street canyon. The measurements were performed under different meteorological conditions (an autumn versus a summer period). A purely physical approach does not provide a true description of reality due to photochemical processes that take place in the street canyon atmosphere. In the summer, sunlight triggers the production of ozone and thereby influences the concentration of NO_2 . The formation of an inverse nondiffuse vertical concentration distribution of NO_2 in the morning hours was found to be related to the direct emission of O_3 in the street and its background concentration. Rapid changes in

NO₂ concentrations were observed over time and in the vertical profile. An approach using a photochemical reactor to describe the processes in a street canyon atmosphere was developed and verified as a useful tool for prediction purposes.

Analyses of the processes related to the dispersion of pollutants in a street canyon were carried out based on the results of comprehensive NO₂ and O₃ concentration level monitoring in the vertical profile above the street. A set of the spatial measurements of the pollutant distribution during a day was realized using the combined DIAL/SODAR method and spot analysers. The measurements were performed under different meteorological conditions (i.e., an autumn versus a summer period). The vertical profiles of NO₂ concentration were interpreted based on a mathematical model developed specifically for the given seasonal conditions (summer period) when diurnal patterns of airborne pollutants in urban street canyons are significantly affected by photochemical processes.

The analysis clearly proved that a purely physical approach does not provide a true description of reality in the given case because the chemical reactions and photochemical processes taking place in the street canyon atmosphere significantly affect the dispersion and distribution of pollutants. An explanation of the inverse NO₂ and O₃ distribution was also provided. The approach of treating a street canyon as a photochemical reactor is valid and is useful for prediction purposes [74-78].

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LIST OF ABBREVIATIONS

MW - MicroWave
 IR - InfraRed
 LIDAR - Light Detection And Ranging
 DIAL - Differential Absorption Lidar
 QC - Quantum Cascade
 HITRAN - High Resolution TRANsmision molecular absorption database
 SODAR - SONic Detection And Ranging
 FTIR - Fourier-Transform InfraRed
 MIR - Mid-InfraRed
 QCLs - Quantum Cascade Lasers
 UV – UltraViolet
 WMS - Wavelength-Modulation Spectroscopy
 FMS - Frequency-Modulation Spectroscopy
 CRDS - Cavity RingDown Spectroscopy
 ICLAS - IntraCavity Laser Absorption Spectroscopy
 NIR - Near-InfraRed
 DFB - Distributed-FeedBack
 ECDL - External Cavity Diode Laser
 OPOs - Optical Parametric Oscillators
 CW - Continuous Wave
 QTFs - Quartz Tuning Forks
 QEPAS - Quartz-Enhanced PhotoAcoustic Spectroscopy
 NNEA - Normalized Noise Equivalent Absorption
 PAS - PhotoAcoustic Spectroscopy

AFM - Atomic Force Microscopy
MLG – Multi-Layer Graphene
SLG - Single-Layer Graphene
HITEMP – High-TEMPerature molecular spectroscopic database
TDLAS - Tunable Diode Laser Absorption Spectroscopy
MEMS - MicroElectroMechanical System
HOPG - Highly Ordered Pyrolytic Graphite
UHV - UltraHigh Vacuum
RADAR - RADio Detection And Ranging
YAG – Yttrium Aluminium Garnet
DASE - Differential Absorption Scattering Energy
BBO - Barium- β -BORate
QSSA - Quasi-Steady State Assumption
ODEs - Ordinary Differential Equations
LT – Local Time

Attachments

List of publications that are part of the presented thesis:

- [1] J. Suchánek, P. Janda, M. Dostál, A. Knižek, P. Kubát, P. Roupcová, P. Bitala, V. Nevrlý, Z. Zelinger, Photoacoustic spectroscopy with mica and graphene micro-mechanical levers for multicomponent analysis of acetic acid, acetone and methanol mixture, *Microchemical Journal*, 144 (2019) 203-208.
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Citation summary for publications that are part of the submitted thesis
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