LABORATORY SPECTROSCOPIC STUDIES OF INTERMEDIATES RELEVANT TO THE COMBUSTION

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LABORATORY SPECTROSCOPIC STUDIES OF REACTIVE INTERMEDIATES RELEVANT TO THE COMBUSTION

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1. Abstract

The goal of this thesis is to describe studies about molecular species investigated by spectroscopic methods which are relevant to the safety sciences – it means first of all chemistry of combustion.

The first chapter called "Microwave spectroscopy of the H2\textsuperscript{12}C\textsuperscript{16}O" deals with molecule of formaldehyde studied by microwave spectroscopic technique, namely rotational transitions within excited vibrational states in the millimeter-wave and submillimeter-wave region. This work has been motivated by the atmospheric and astrophysical importance of formaldehyde (H\textsubscript{2}CO). The main aid of this study is to complete the already existing list of rotational transitions within the ground vibrational state by a list of transitions within the four first excited 2\textsuperscript{1}, 3\textsuperscript{1}, 4\textsuperscript{1} and 6\textsuperscript{1} vibrational states, to help the detections of this species by microwave or millimeterwave techniques.

In the second chapter called "Photoacoustic spectroscopy of the C\textsubscript{7}H\textsubscript{14}O\textsubscript{2}" are interpreted absorption spectra of molecule of n-pentylacetate studied by photoacoustic detection (PAS) for concentration analysis. The absorption spectra of gaseous n-pentylacetate has been investigated by means of Fourier transform infrared spectroscopy (FTIR) as well as CO\textsubscript{2}-laser photoacoustic spectroscopy (PAS) for simulation of the dispersion of a nerve agent (sarin) within a modeled atmospheric boundary layer. Three CO\textsubscript{2}-laser emission lines has been used for photoacoustic detection of n-pentylacetate with detection limit in the range of 1-3 ppm.

And the last chapter called "Infrared spectroscopy of XCN" deals with molecular ions from CN\textsuperscript{•} radical family, especially halogen-cyanide radical cations XCN\textsuperscript{+} (X = Br, I, Cl) studied by use of tunable diode-laser (TDL) infrared spectroscopic technique. Radical cation ICN\textsuperscript{+} has been studied theoretically and also experimentally by means of this method as well as by means of the FTIR spectroscopy in the discharge plasma as a simulation of exothermic medium. Series of the lines with periodic wavenumber distances have been detected. It is supposed that they indicate new generated species that has been proved by Loomis Wood analysis. Furthermore the FTIR spectra have been recorded and individual bands have been assigned to determinate the chemical composition of the newly generated species at discharge conditions.

Keywords: safety sciences; spectroscopy; chemistry of combustion
2. Abstrakt

Cílem této disertační práce je charakteritka molekulárních iontů významných z hlediska bezpečnostních věd, což znamená především chemie hoření, vyšetřovaných pomocí vybraných spektroskopických metod.

První kapitola nazvaná “Microwave spectroscopy of the $\text{H}_2\text{^{12}}\text{C}^{16}\text{O}$” se zabývá mikrovlnnými spektrometry molekuly formaldehydu, přesněji rotačními přechody v rámci excitovaných vibračních stavů v milimetrové a submilimetrové oblasti elektromagnetického spektra. Tato studie byla motivována atmosférickou a astrofyzikální důležitostí formaldehydu ($\text{H}_2\text{CO}$) a jejím hlavním cílem bylo doplnění již existujícího přehledu rotačních přechodů v rámci základního vibračního stavu molekuly o zcela nový soupis přechodů v rámci čtyř prvních excitovaných vibračních stavů $2^1, 3^1, 4^1$ a $6^1$ k zlepšení detekce této spécie pomocí metod mikrovlnné či milimetrové spektroskopie.

Ve druhé kapitole nazvané “Photoacoustic spectroscopy of the $\text{C}_7\text{H}_{14}\text{O}_2$” jsou interpretována absorpční spektra molekuly n-pentylacetátu zkoumaná metodou optoakustické spektroskopie (PAS) ke koncentrační analýze. Absorpční spektra plynného n-pentylacetátu byla zkoumána infračervenou spektroskopii s Fourierovou transformací (FTIR) a zároveň CO$_2$-laser optoakustickou spektroskopii (PAS) ke přímé kvantitativní spektroskopické detekci stopových množství plynu a následně využití této metody při experimentech fyzikálních simulací šíření zástupce nervového plynu (sarinu) uvnitř modelované mezní vrstvy atmosféry v nízkorychlostním aerodynamickém tunelu.

A poslední kapitola nazvaná “Infrared spectroscopy of XCN” se zabývá studiem molekulárních iontů z řady CN$^-$ radikálů, především halogen-kyanidových radikálových kationtů XCN$^+$ (X = Br, I, Cl) s použitím metod laditelné laser-diodové (TDL) infračervené spektroskopie. Radikálový kation ICN$^+$ byl studován teoreticky a experimentálně pomocí této metody, stejně tak pomocí FTIR spektroskopie, v nízkoteplotním výbojovém plazmatu jako simulace exotermického prostředí. Byla detekována řada linek s pravidelným vlhčtovým rozestupem, které pravděpodobně indikují nové spécie vznikající ve výboji, což bylo provedeno analýzou v programu LoomisWood. Dále byla zaznamenána FTIR spektpra a byly přiřazeny jednotlivé pásy k přesnějšímu určení chemického složení nově generovaných spécií ve výbojových podmínkách.

Klíčová slova: bezpečnostní vědy; spektroskopie; chemie hoření
3. Summary

The title of presented work “Laboratory spectroscopic studies of reactive intermediates relevant to the combustion” describes its motif as well. It is complex of studies using spectroscopic methods to measure diverse species under the laboratory conditions. The species which are somehow interesting from the combustion and burning processes point of view together with the processes producing toxic species. The assortment of studied molecules in gas phase represents intermediates and terminal products of mentioned processes that can be both reactive or stable particles, they are further more relevant from the point of view of combustion chemistry, atmospheric chemistry and last but not least astrochemistry. The text itself is topically divided to the three chapters according to every individual study.

The first chapter called “Microwave spectroscopy of the H212C16O” deals with molecule of formaldehyde studied by microwave spectroscopic technique, namely rotational transitions within excited vibrational states in the millimeter-wave and submillimeter-wave region. This work has been motivated by the atmospheric and astrophysical importance of formaldehyde (H2CO). The main goal of this study has been to complete the already existing list of rotational transitions within the ground vibrational state by a list of transitions within the four first excited 21, 31, 41 and 61 vibrational states, to help the detections of this species by microwave or millimeterwave techniques. For this purpose, the rotational spectra of H2CO in the 21, 31, 41 and 61 excited vibrational states have been investigated in Lille and Cologne in the millimeter region at 160 – 600 GHz and 850 – 903, respectively. The results of these measurements has been than combined with the 21, 31, 41 and 61 infrared energy levels, which has been obtained from previous analysis of FTS spectra of the ν4, ν6 and ν3 bands recorded in 10 μm region and more recently for the ν2 fundamental band. The energy level calculation of the 21, 31, 41 and 61 interacting states accounts for the various Coriolis-type resonances that perturb the energy levels of the 21, 31, 41 and 61 vibrational states as well as for the anharmonic resonances coupling the 21 and 31 energy levels, and in this way the microwave and infrared data could be reproduced within their associated experimental uncertainty. However, it is clear that the theoretical model used to account for the very large A-type Coriolis resonance linking the 41 and 61 energy levels of H2CO is only effective with poor physical meaning. This study has been solved and also partially treated in the Laboratory of laser, atom and molecular physics, at the University of Sciences and Technologies Lille 1 in France within international project QUASAAR (Quantitative Analysis for Atmospheric and Astrophysical Research) under the leading of prof. Georgès Wlodarczak and Dr. Laurent Margulès, where my research work has been performed within the study so-called „doctorat en co-tutelle“ – „doctorate under joint supervision“.

In the second chapter called “Photacoustic spectroscopy of the C7H14O2” are interpreted absorption spectra of molecule of n-pentylacetate studied by photacoustic detection (PAS) for concentration analysis. Gaseous n-pentylacetate (n-amylacetate) has been recently employed in dispersion studies instead of sarin (C4H10FO2P). An extremely toxic nerve agent is represented by a non-toxic tracer with similar physical – chemical characteristics such as vapor pressure, boiling point or molecular mass. The absorption spectra of gaseous n-
pentylacetate has been investigated by means of Fourier transform infrared spectroscopy (FTIR) as well as CO2-laser photoacoustic spectroscopy (PAS) for simulation of the dispersion of a nerve agent (sarin) within a modeled atmospheric boundary layer. An FTIR spectra has been recorded by the Bruker IFS 120 spectrometer within a range of 600 – 2000 cm⁻¹ confirmed the absorption maximum around 1240 cm⁻¹ corresponding to the C-O stretch. The spectral region available for PAS detection (9-11µm) is characterized by a broad and weak absorption band of n-pentylacetate. Three CO2-laser emission lines has been used for photoacoustic detection of n-pentylacetate with detection limit in the range of 1-3 ppm. These concentration levels are expected in wind tunnel modeling dispersion experiment. A generation of trace amounts of n-pentylacetate has been obtained by the use of precise concentration standards based on the permeation method, standards were made of polyethylene and Teflon tubes. Based on all available information the CO2-laser photoacoustic spectrum of gaseous n-pentylacetate has been recorded for the first time. This study has been solved partialy at the Faculty of Safety Engineering, VŠB – Technical University of Ostrava and partially at the dispersal compartment of Institute of Thermomechanisc in Nový Knin under the scientific leading of prof. Ing. Zdeněk Zelinger, CSc.

And the last chapter called “Infrared spectroscopy of XCN⁺” deals with molecular ions from CN⁺ radical family, especially halogen-cyanide radical cations XCN⁺ (X = Br, I, Cl) studied by use of tunable diode-laser (TDL) infrared spectroscopic technique. Radical cation ICN⁺ has been studied theoretically and also experimentally by means of this method as well as by means of the FTIR spectroscopy in the discharge plasma as a simulation of exothermic medium. The molecular ions are important species from the point of view of its existence and they are considerable subject of research in the field of chemistry, physics and astronomy. The tunable diode laser (TDL) infrared spectroscopy has been proved as a sufficiently effective and sensitive for the detection of free radicals and molecular ions. The intimate study of the fundamental band of BrCN⁺ molecule has been performed by means of this method in infrared region. However, the corresponding studies of ICN⁺ and ClCN⁺ have not been done up to the present time. The spectroscopic constants of mentioned radical ions are unknown or partially known, and therefore we onward proposed spectroscopic searching of rotational-vibrational transitions of these ions. The knowledge of the infrared spectra of studied ions is a necessary precondition for subsequent research in the range of microwave spectroscopy. The TDL absorption infrared spectroscopic method has been applied for the open study of radical cation ICN⁺ in the region about 2080 cm⁻¹, which is corresponding to middle of the band according to the previous studies. This experiment has been supplemented by the high resolution Fourier transform infrared (FTIR) spectroscopy. Since the TDL infrared spectroscopy provides sensitivity and the FTIR spectroscopy provides broad spectral range, these methods have been selected for investigation of combustion and burning processes including production of reactive intermediates and terminal products. The both of these explorations have been performed in the discharge plasma to simulate an exothermic medium. The hollow cathode discharge has been used in case of TDL spectroscopy. Series of the lines with periodic wavenumber distances have been detected. It is supposed that they indicate new generated species that has been proved by Loomis Wood analysis. Furthermore
the FTIR spectra have been recorded and individual bands have been assigned to
determine the chemical composition of the newly generated species at discharge
conditions. The microwave discharge has been used for the experiment by FTIR
spectrometer. This study has been performed under the scientific leading of prof.
Ing. Zdeněk Zelinger, CSc. at the nursery of Heyrovsky Institute of Physical
chemistry of CAS, which has an agreement about collaboration with the Faculty of
Safety Engineering, VŠB – Technical University of Ostrava.

All the experimental as well as theoretical backgrounds of dissertation have
been solved and treated within internation collaboration in between Faculty of
Safety Engineering, VŠB – Technical University of Ostrava and Laboratory of
lasers, atoms and molecular physics, University of Sciences and Technologies
Lille 1 in France. This collaboration is great contribution for the subject field “Fire
protection and industrial safety” not only due to availability of modern
spectroscopic technics.
4. Contents

1. Abstract .................................................................................................................. 3
2. Abstrakt ................................................................................................................... 4
3. Summary .................................................................................................................. 5
4. Contents .................................................................................................................. 8
5. General Introduction ............................................................................................... 11
6. Microwave spectroscopy of the H₂CO .................................................................. 13
   1.1. Introduction ........................................................................................................ 13
   1.2. Motivation and previous studies ........................................................................ 15
   1.3. Atmospheric interest ......................................................................................... 15
   1.4. Astrophysical interest ....................................................................................... 15
   1.5. Spectroscopic interest ....................................................................................... 15
   1.6. Results and discussion ..................................................................................... 16
7. Photoacoustic spectroscopy of the C₇H₄O₂ .............................................................. 18
   1.7. Introduction ........................................................................................................ 18
   1.8. Motivation and previous studies ........................................................................ 18
   1.9. Results and discussion ..................................................................................... 19
8. Infrared spectroscopy of XCN⁺ .............................................................................. 21
   1.10. Introduction ...................................................................................................... 21
   1.11. Motivation and previous studies ..................................................................... 21
   1.12. Results and discussion ................................................................................... 23
9. Conclusion ................................................................................................................ 27
10. Related publications .............................................................................................. 27
11. Bibliography .......................................................................................................... 28
12. Seznam publikací .................................................................................................. 30
13. Seznam konferencí ................................................................................................. 31
Goals of the thesis

A formulation of particular studies concerning present work is listed below:

✓ Realization of a bibliographic search concerning theoretical computations and experimental measurements of rotational transitions of the ground vibrational state of formaldehyde molecule H\textsubscript{2}CO and its isotopomers (e.g. H\textsubscript{2}\textsuperscript{13}C\textsuperscript{16}O and H\textsubscript{2}\textsuperscript{12}C\textsuperscript{18}O) in the gas phase.

✓ Implementation of the methodology for spectral measurements using the molecules of CH\textsubscript{3}CCl\textsubscript{3} and HCOOCH\textsubscript{2}D as examples by means of a microwave spectrometer. Description of the experimental setup, its individual parts, their corresponding functions and basic operational principles. Subsequent description of optimization of conditions for production and detection of H\textsubscript{2}CO in the gas phase.

✓ Based on the prediction of rotational frequencies (obtained by means of \textit{ab initio} calculations of molecular constants within the scope of other theoretical studies) perform a measurement using the Lille MMW spectrometer in millimeter and submillimeter range (150-660 GHz). First in the ground vibrational state for the sake of experimental optimization and subsequently in the first excited vibrational state.

✓ Evaluate the experimental data in order to obtain the values of rotational frequencies of the highly resolved spectral lines of H\textsubscript{2}CO in the gas phase. Describe the potential applications of the results within the field of molecular spectrometry and astrophysics and within the context of fire protection and industrial safety management.

✓ Carry-out of the bibliographic search concerning the means of exploitation of the method of photoacoustic detection in the field of safety engineering - particularly its use for monitoring of dangerous chemical substances in gaseous phase. Carry-out of the publication search concerning similarities between the model molecule of n-pentylacetate and the molecule of Sarine.

✓ Scan of the entire spectral range of the n-pentylacetate by means of the FT IR. Build-up and tuning of the laser photoacoustic experimental setup, preparation of the concentration standards of the model gas n-Pentylacetate and final measurement of concentrations using selected emission lines of the CO\textsubscript{2}-laser.
Evaluation of the experimental results, calculating of the detection limit and the quantification limit of the analyzer. Description of potential applications of the obtained results and their implementation in simulation of the spread of one representative of the neurotoxic gas family (Sarine) within simulated boundary layer of the atmosphere.

Realization of publication search on the topic of molecular ions, above all cations - the unstable radical species that play significant role in the environments of flames and physical plasmas - by means of various spectroscopic techniques. Study of XCN⁺ (X = Br, I, Cl) radical cations, members of the group of CN• radical ions.

Set-up and optimization of the laser-diode spectrometer, description of the involved experimental arrangement. Study of the radical cation BrCN⁺, which was not carried out with enough detail in the IR range in the past. Calibration of the experimental apparatus using the known lines of the BrCN⁺.

Search for further lines of significant unstable species in the IR spectrum, e.g. those of CN• radical and BrCN⁺ ion. Consecutive search for up-to-now not-measured spectral lines of radical cations ICN⁺ a CICN⁺. Preparation and test of precursors.

Methodology of the thesis

Several spectroscopic methods were used to aid in reaching the goals of this work. The methods, in order of nominal appearance of corresponding studies in the section Summary - are listed below:

1. Microwave and millimeter spectroscopy,
2. CO₂-laser photoacoustic spectroscopy (PAS)
3. Laser-diode absorption spectroscopy.
5. General Introduction

The high resolution molecular spectroscopy (HRMS) is a relatively young and thus modern scientific branch of knowledge that is closely related to the natural sciences and consequently also to the branches of fire protection and industrial safety. The spectroscopy, apart from other things, strongly contributes to the development of all these branches that come under the safety engineering disciplines. Since the experimental molecular spectroscopy together with the theory provide us the information about the molecular structure, the development in many other scientific branches such as, for example, atmospheric chemistry and astrochemistry is based on results of the molecular spectroscopy. With respect to objectives and orientation of the Department of Fire Protection it is, first of all, chemistry of combustion, studies of the processes in the flames, or also monitoring of dangerous chemical matters in the gas phase, where the spectroscopy can significantly contribute with the help of modern experimental techniques.

One of the fundamental and still open tasks of Safety Engineering is characterization of physical-chemical effects related to the combustion, processes of matter burning and processes producing toxic species. The characteristic properties of flame burning of matter are connected with chemical composition in the relevant process as, for example, chemical composition of the flames. The components of such processes are as well intermediates (e. g. ions in plasma) and terminal products (e. g. product of combustion as the atmospheric pollution) of combustion. Toxic intermediates of combustion can be both reactive and stable particles. The essential role in the processes, that are asserted in flame burning of matter and their extinguishing, play reactive unstable particles, in the first place radicals and in many cases also ions, as well as stable particles in a combustion product form. These particles are further related to the contaminated atmosphere by trace amount of manifold gaseous pollutants that has subsequently also huge impact on the environment. It is possible to clarify these phenomena of the individual burning and extinguishing processes with the aid of laboratory experiments, where one can study isolated elementary reactions with the possibility of spectroscopic monitoring.

Nowadays, physical methods primarily based on spectroscopic methods are very often applied for detection of the molecules in gas phase. The study and measurement of the absorption, emission or scattering of the electromagnetic radiation by matter as a function of the wavelength, wave number or frequency of the radiation, is the subject of spectroscopy. On the basis of the fact that each atom and molecule has the unique spectrum, the spectroscopy is the most important source of information about the composition of the matter and also the atomic or molecular properties that has broad range of application in all fields of chemical research – qualitative and quantitative analysis. The complete knowledge of the spectral characteristics is necessary precondition for monitoring, which is often exploited of late in the safety engineering, for example, in the study of dangerous chemical species in the gas phase formation and the like. Spectroscopic methods are suitable for the concentration analysis of the gas phase composition under laboratory conditions as well as for direct detection in the free atmosphere. This is very important for the risk estimation and for the security
and safety research, among others even for the prevention of environmental disasters.

The practical application of the spectroscopic methods to study of radicals and ions then require high sensitivity and resolution. The high sensitivity is important for the reason of short life times and relatively low concentrations of radicals and ions, and high resolution enables unambiguous identification of individual species, i.e. selectively distinguish lines of different radicals and lines of mother molecules.

The spectroscopic measurements are carried out in all regions of the electromagnetic radiation, i.e. from radio waves to gamma rays. The following chapters are focused on the molecular absorption spectroscopy of gaseous samples in the millimeter-wave, submillimeter-wave and infrared region, in the area where the pure rotational, rotational-vibrational and vibrational transitions are observed and studied.
6. Microwave spectroscopy of the $\text{H}_2\text{CO}$

This chapter deals with the molecule of formaldehyde studied by microwave spectroscopic technique, namely rotational transitions within excited vibrational states in the millimeter-wave and submillimeter-wave region.

This work has been motivated by the atmospheric and astrophysical importance of formaldehyde ($\text{H}_2\text{CO}$). The main goal of this study has been to complete the already existing list of rotational transitions within the ground vibrational state by a list of transitions within the four first excited 21, 31, 41 and 61 vibrational states, to help the detections of this species by microwave or millimeterwave techniques. For this purpose, the rotational spectra of $\text{H}_2\text{CO}$ in the 21, 31, 41 and 61 excited vibrational states have been investigated in the millimeter region at 160 – 600 GHz.

This study has been solved and also partially treated in the laboratory of the Lille 1 University in France within the international project scholarship QUASAAR under the leading of prof. Georgés Wlodarczak and Dr. Laurent Margulé. In this study I have participated mainly the experimental part.

1.1. Introduction

Molecular spectra have previously been well described from the point of view of infrared spectroscopy (Chapter III.) – but the different frequency range, higher resolution, and greater accuracy of microwave spectroscopy makes available for study rather different types of phenomena such as for example hyperfine structure, pressure broadening, and Stark or Zeeman effects.

High-resolution rotational spectroscopy is a technique that is used mainly to detect molecules in the gas phase. It is a unique method based on the foundations of quantum mechanics. The study of the interaction of microwave and submillimeter electromagnetic radiation with the molecular environment delivers a detailed knowledge of the spectral, chemical and quantum mechanical properties of molecules and molecular fragments. Thanks to a very sophisticated theory of microwave spectroscopy, these findings may be analyzed and simulated in order to obtain key spectroscopic information necessary for the interpretation of atmospheric and astrophysical measurements. Detailed characterization of the molecular structure of the model substance also contributes to the explanation of the phenomena in chemical reactions and, of course, the processes of combustion or fire suppression. Specific spectroscopic characteristics obtained by studying the rotational transitions of molecules on this model allows to continue the study of molecules of a similar type. The object of rotational spectroscopy is the study of spectroscopic transitions between quantum states of molecules that differ only by the rotational quantum numbers, i.e. spectroscopic transitions, during which there is no change in vibrational or electronic state, mainly within the limits of the basic vibrational and basic electronic states. In this study, however, we also deal with rotational transitions within the first excited vibrational states.

When measuring the rotational structure of the energy levels of the examined molecule, its rotational movement must be sufficiently free; therefore,
we can speak mainly about the spectroscopy of gases or substances that can convert into a gas phase. The energy differences between the different rotational states are usually significantly less than those between the different vibrational or even electronic states. While the electron spectra are usually observable in the visible and ultraviolet regions (UV, VIS) and the vibrational spectra in the infrared region (IR), the differences between the rotational levels usually correspond to the so-called "microwave" region of the spectrum (MW). This area is situated between the infrared and radio frequency areas, i.e., in the field of frequencies from 300 MHz up to hundreds of gigahertz (GHz), as shown in the (Figure 6-1). The interval expressed in wavelengths has a range from tenths of a millimeter to tens of centimeters.

![Figure 6-1: The electromagnetic spectrum classified according to the radiation wavelengths, wavenumbers, electron volts and frequencies.](image)

The spectrum obtained during the experiments in the microwave region of the electromagnetic radiation is a graphical representation of the detected intensity of energy in relation to the energy frequency. In microwave spectroscopy, the most commonly used unit is Hertz (see section Error! Reference source not found.). However, often it may be useful to know the relations between various units used by other spectroscopies in different regions of electromagnetic radiation (Figure 6-1).
1.2. Motivation and previous studies

Formaldehyde is one of the most extensively studied molecule which is playing important role in the atmospheric chemistry, chemistry of combustions, photochemistry of the troposphere etc. – there are many reasons for its interest. One of the goal of present study is to have a more complete description of the millimeter-wave and submillimeter-wave spectrum in the excited vibrational states for possible astrophysical applications.

Formaldehyde (methanal) is the chemical compound with the formula H$_2$CO. The simplest aldehyde, it was first synthesized by the Russian chemist Aleksandr Butlerov but was conclusively identified by August Wilhelm von Hofmann. Formaldehyde exists several forms acide from H$_2$CO: the cyclic trimer trioxane and the polymer paraformaldehyde. Additionally it exists as the hydrate H$_2$C(OH)$_2$ in water.

The reliable prediction of rotational spectra of formaldehyde is important from several points of view – atmospheric, astrophysical and spectroscopic point of view:

1.3. Atmospheric interest

Formaldehyde is an intermediate in the oxidation or combustion of methane as well as other carbon compounds. It can be found in the smoke from forest fires, in automobile exhaust, and in tabacco smoke. In the atmosphere, formaldehyde is produced by the action of sunlight and oxygen on atmospheric methane and other hydrocarbons. It thus becomes part of smog pollution. Small amounts of formaldehyde are produced as a metabolic by product in most organisms, including humans. As the one of the toxic intermediates of combustion the formaldehyde has a huge impact on environment and human health.

1.4. Astrophysical interest

From the astrophysical point of view, the formaldehyde is one of the most abundant and one of the first polyatomic molecules detected in interstellar clouds (at first in 1968) and it was indentified in several cometary objects mostly at millimeter wavelengths – all of the formaldehyde isotopic species has been detected (e. g. it was observed in Orion molecular clouds or low-luminosity protostar Ira). The molecule of formaldehyde is also associated with theories about the origin of life on the Earth.

1.5. Spectroscopic interest

From the spectroscopic point of view it is then necessary to have accurate experimental data to verify the accuracy of ab initio calculation. The molecule of formaldehyde consists of four atoms and thus it is relatively small light tetraatomic molecule with the large rotational constants and relatively large dipole moment (µ=2,3D). Therefore it also has a strong submillimeter spectrum. It is possible to verify convergency of Watson Hamiltonian thanks to this model molecule. The
formaldehyde is hence the key to our understanding of spectroscopy of polyatomic molecules – the model approximates a description of reality.

1.6. Results and discussion

The main problem, which partly impeded the achievement of results in the experimental part of the study, was specifically the problem of very low intensities of the lines in the first excited vibrational states. Error! Reference source not found. shows the specific lines that were measured with the Lille spectrometer in the area of 150 to 660 GHz and that make obvious the problem with the line intensity. The lines with the highest intensity lie in the frequency region around 400 GHz to 650 GHz, but there are only few of them (designated by arrows in the image); most of the lines, on the other hand, have a very low intensity. Such data of lines with the intensity problem is very difficult to process: two lines of this type that are almost merging with the noise can be seen on Error! Reference source not found.. Therefore, it is appropriate to perform a few repetitions and to take into account the inaccuracy of measurement when verifying the data in the program [12]. The intensity problem often arises also in marginal areas of measuring tubes, where it is further boosted by the overall instability of the measuring equipment.

Figure 6-1: The real lines of formaldehyde measured in Lille, the most intense lines are shown by green arrows.

Figure 6-2: The concrete recorded lines of formaldehyde in the first vibrational excited state – very low intensity and unstable background of the spectrometer.
Another interesting feature is the possible presence of various isotopic forms of carbon, which can, however, cause more difficulties in processing the spectra. If we tune the specific area where we expect the line to be in accordance with our precalculated values and two lines appear on the site that have similar frequency distance and similar high intensity, it means we have a problem with the determination, which of these two lines actually matches the sought transition and whether it corresponds to our substance at all (Fig. 10-2). One of the possible reasons may be the presence of a line of another isotope, which happened in our study, where it was the presence of formaldehyde with an isotope of carbon 13C, i.e., the molecule H213C16O (the line in the image marked with an arrow). Since 13C is a stable isotope of carbon and its natural amount is around 1.1% of the total amount of natural carbon (all isotopes) on Earth, it is quite likely that we can come upon this isotope also in the spectrum (note: of the 100 measured lines, roughly one line may belong to the isotope 13C). This fact can be verified by using the free database of the JPL Molecular Spectroscopy catalogue of the NASA Jet Propulsion Laboratory, California Institute of Technology.

Figure 6-3: The concrete recorded lines of formaldehyde – two different isotopic species.
7. Photoacoustic spectroscopy of the C_{7}H_{14}O_{2}

1.7. Introduction

The CO2-laser photoacoustic detection technique is a suitable spectroscopic method for analysis of the concentration of substances in gas phase applicable both in laboratory conditions and for direct detection in the ambient atmosphere. It is therefore very useful, for example, for detection of harmful substances, monitoring of their spread in the atmosphere, which is often used in safety engineering.

In this part of the study, the absorption spectra of n-pentyl acetate in the gas phase were explored using Fourier transform infrared spectroscopy (FTIR) and CO2-laser photoacoustic spectroscopy (PAS) for subsequent simulation of the spread of matter representing the nerve gas (sarin) inside of the boundary layer of the modelled atmosphere. For the photoacoustic detection of n-pentyl acetate in the gas phase, three emission lines of CO2-laser with a detection limit 1-3 ppm were used.

1.8. Motivation and previous studies

The species studied in this chapter is a molecule of n-pentylacetate and it is appropriate to mention why the study with this molecule was conducted. The very substance of the gaseous n-pentylacetate (n-amyl acetate; C7H14O2) was already in the past and also recently used in dispersion studies [13] instead of the nerve gas sarin (C4H10FO2P), which was one of the motivational factors of this study. The extremely toxic substance, which is used as a nerve gas, is represented here by its non-toxic substitute with similar physico-chemical properties, such as vapor pressure, boiling point and molecular weight. Another motivation for this study was the possible use of photoacoustic spectroscopic technique for the analysis of the trace amount of gas and subsequent use for modeling experiments simulating the spread of gaseous substances inside the wind tunnel [14]. As the tools for various simulations, such models of nerve gases are very important for risk assessment and research in safety engineering.

In fact, there are only a few spectroscopic studies on n-pentyl acetate in gas phase in the infrared region of the spectrum [15-17], however, these are primarily experimental studies carried out using the Fourier transform infrared spectroscopy technique; some further information can be obtained from the NIST database [18]. There was another diffusion study that used physical modeling for simulating the spread of toxic substance (its substitute) and included visualization of its diffusion in urban area, namely, the Old Town Square in Prague in a scale of 1:160 (urban scale) [13], where the choice of the substituent and the similarity of the two molecules are also described quite thoroughly. Based on all available information it can be said that the CO2-laser photoacoustic spectrum of n-pentyl acetate in gas phase was recorded for the first time.
1.9. Results and discussion

The CO2-laser photoacoustic absorption spectrum of gaseous n-pentylacetate (C7H14O2) has been investigated and recorded for the first time, on the basis of all available information. In this work, detection limit and limit of determinableness has been determined from calibration curves acquired on three relatively strong emission lines of CO2-laser. The PAS (photoacoustic spectroscopy) experiment has been prepared for subsequent utilization as the online quantitative spectroscopic detection within the framework of physical simulations of the dispersion inside the modeled atmospheric boundary layer [14]. The n-pentylacetate has been used as a non-toxic substituent with similar physical-chemical characteristic of sarin (C4H10FO2P).

![Figure 7-1: High resolution absorption spectrum of n-pentylacetate – screening specifically through the spectral region 9-11 μm (available for PAS detection) by the FT IR method, enlarged section see on the right.](image)

![Figure 7-2: The absorption spectrum of gaseous n-pentylacetate appointed with the aid of photoacoustic method (PAS) on the emission lines of CO2-laser.](image)
Figure 7-3: Calibration curves for calculations of detection limit and the quantification limit (Tab. 1) - dependence of standardized photoacoustic signal on concentration, acquired amount about 10 – 300 ppm.

<table>
<thead>
<tr>
<th>CO₂-laser emission lines</th>
<th>detection limit [ppm]</th>
<th>limit of determinableness [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9P(20)</td>
<td>1.37</td>
<td>4.55</td>
</tr>
<tr>
<td>9P(22)</td>
<td>2.05</td>
<td>6.82</td>
</tr>
<tr>
<td>9P(24)</td>
<td>2.55</td>
<td>8.33</td>
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</table>

Table 7-1: Table of detection limits and limits of determinableness on the selected CO₂-laser emission lines.
8. Infrared spectroscopy of XCN⁺

1.10. Introduction

Molecular ions, with regard to their occurrence, are an important object of research in the fields of chemistry, physics, and astronomy. From the available information, it is known that several spectroscopic studies of the molecular ions and the reaction of ions with molecules have been carried out. Following these previous studies and aiming to expand them, this project deals with the study of the ions of CN radicals, radical cations XCN⁺ (X = Br, I, Cl). Tunable infrared spectroscopy has proven to be an effective and sensitive method of detection of free radicals and molecular ions. The first study of the basic band BrCN⁺ in IR was carried out with its use, but not the corresponding studies for ICN⁺ and CICN⁺. Obtaining infrared spectra of the studied ions would be a great help for subsequent unique measurements in the area of microwave spectroscopy.

In this study the tunable diode laser (TDL) absorption infrared spectroscopic method has been applied for the open study of radical cation ICN⁺ in the region about 2080 cm⁻¹, which is corresponding to middle of the band according to the previous studies. This experiment has been supplemented by the high resolution Fourier transform infrared (FTIR) spectroscopy. Since the TDL infrared spectroscopy provides sensitivity and the FTIR spectroscopy provides broad spectral range, these methods have been selected for investigation of combustion and burning processes including production of reactive intermediates and terminal products. The both of these explorations have been performed in the discharge plasma to simulate an exothermic medium. Our experimental arrangement is described later on.

1.11. Motivation and previous studies

Molecular ions and especially cations are important species on Earth and in space, in the environments such as flame, plasma, comets, the atmosphere of planets, interstellar space etc. [23]. This is the reason why molecular ions attract the attention of chemists, physicists and astronomers. Many spectroscopic studies of the molecular ions and the reaction of ions with molecules have been carried out [24].

Tunable infrared spectroscopy has proven to be an effective and sensitive method of detection of free radicals and molecular ions. The detection of small concentrations and weak absorption during spectroscopic studies of molecular ions requires the use of the methods of phase-sensitive detection of the type of speed modulation and especially production modulation [25]. It is the production modulation in hollow cathode discharges that has proven to be very promising in the spectroscopic research of the radicals and ions containing carbon and nitrogen [26]. Therefore, the production of radical cations XCN⁺ (X=Cl, Br, I) in a hollow-cathode discharge with the XCN precursor and Penning ionization using atoms of helium was designed for this study. Spectroscopic constants of the mentioned radical ions are either known only partially or unknown; therefore, the
spectroscopic search for rotational-vibrational transitions of these ions was included in the study. Spectroscopy in neon matrices has provided optical absorption spectra of gradients B 2[\Pi]3/2 ← X 2[\Pi]3/2 of the cations XCN+, transitions A 2Σ+ ← X 2[\Pi]3/2 of the cations ICN+, absorption bands of CN· radical in the spectra CICN+ and BrCN+ and infrared spectra of the cations ICN+. The electronic spectra of radical cations XCN+ has been studied using the emission spectroscopy with excitation in the gas phase by electron bombardment. Using the emission spectroscopy of supersonically cooled XCN+ the transitions corresponding to vibrational structures have been gradually assigned. The first study of the basic band BrCN+ using the IR laser-diode spectroscopy was carried out, but not the corresponding studies for ICN+ and CICN+. The vibrational frequency of XCN+ in basic electronic states, and also in some excited states have been predicted using the studies based on electron spectroscopy [27]. This data is a very high-quality prediction for search in the infrared region. For this study, the investigations of the infrared region were proposed to be carried out using the sensitive laser-diode spectroscopy with possible use for millimeter and submillimeter spectroscopy.

This study about the radical cation ICN+ is a follow-up to a previous research into the molecule BrCN+ [28]. Bromocyane radical ion (cation BrCN+), which falls into the group of molecules with 15 valence electrons has been experimentally studied in the past (given the objectives of the project to produce, measure and identify the lines of ion radicals, the overview is focused only on experimental studies). The beginning of the study of this molecule dates back to the year 1955 [8]. Due to the low concentrations, and thus small intensities of the absorption lines, the first results of the detection of this ion were unusable for a more detailed characterization, as well as for the calibration accuracy we are seeking. This, however, was an important piece of knowledge for further studies, in which it has proven necessary to use the techniques like phase-sensitive detection. This technique has been also used to observed first high-quality emission spectral lines of BrCN+ in 1976 [29]. In further spectral measurements that used this technique the spectral transitions A2Σ+ → X2Π and B 2Σ → X2Π were identified using photoelectron spectroscopy [30]. To minimize creation of by-products, in both cases a commercial substance of relatively high purity, the radical cation BrCN+ (Sigma-Aldrich, purity 98%) was used as a precursor. Three low-resolution electron belts of the cation radical BrCN+ were measured with spectroscopy using a matrix of the carrier gas neon [31]. The first vibrational spectra of two transitions have been identified in 1985 using emission spectroscopy using supersonic cooling to minimize the intensity of by-products [32]. The result of this valuable study was determination of vibrational frequencies of BrCN+ in the Ω = 3/2 component X2Π (the basic electronic state) and several excited states. Also for the first time the value of the constant spin-orbit interaction of the unpaired electron with other electrons in the molecule was determined at 1477 cm⁻¹. This was followed by the first rotationally resolved study of this ion using the technique of laser excitation [33] and the results of the measurements for the first time determined the approximate structural parameters of the radical ion. Infrared spectroscopy with diode laser as a source of radiation for obtaining precise data from the medium infrared region was not applied until 1993 [28]. The study yielded very valuable results that can be qualitatively considered an objective of this research and that can be used with minimum error for calibration.
of the experiment we conducted, which is very similar in its structure to the one referred to in the mentioned study.

The result of the research is the appropriateness of use of the commercial precursor for the production of the radical ion in a quantity sufficient for the medium infrared region of the electromagnetic radiation using the technique of phase-sensitive detection and the comparison of measurements with the results of the last-mentioned study.

1.12. Results and discussion

Although we have expected the ICN+ production according to the Penning ionization effect in the helium hollow cathode discharge and incidence of this ion in the region around 2082 cm⁻¹ corresponding to the v1 vibrational mode (C-N stretch), we have acquired the set of new lines with periodic wavenumber distances. This spectrum has been recorded with the use of ICN as a sample by means of diode-laser infrared spectroscopy, and obtained lines have been verified as reaction products of this molecule in the hollow cathode discharge with helium, i.e. the lines are not visible without the precursor or without the discharge. The calibration of the obtained lines has been done with aid of well known published lines of the reference gas OCS Figure 8-1.

Figure 8-1: The illustration of the lines measured by means of diode-laser spectroscopy with the precursor of ICN in discharge plasma conditions and stable reference system of OCS.
To easily identify the unknown species, we start up experiment using the Fourier transform infrared spectroscopy to get broad spectral range going on the exothermic conditions. We have expected detection of the lines obtained by diode-laser spectroscopy in the FTIR spectra. However, in spite of the much broader spectral range which the Fourier transform spectroscopy provides, this method is not as sensitive as diode-laser spectroscopy and for that reason we could not see our previously obtained lines using the TDL.

The infrared absorption spectrum of pure ICN molecule and as well the ICN at microwave discharge has been investigated by means of Fourier transform spectroscopy (Figure 8-2 and Figure 8-3). The two different spectra have been obtained and the fundamental $\nu_3$ band corresponding to the C-N stretch with middle of the band at 2179 cm$^{-1}$ [37] has been identified in our study (Figure 8-2). The absence of this band in the spectra of ICN measured in microwave discharge demonstrates evident changes in the chemical processes at exothermic conditions (Figure 8-3). Furthermore, the HCN and HNCO (isocyanic acid) spectrum has been identified as a product of ICN (Figure 8-2) and ICN with helium discharge (Figure 8-3). The helium discharge spectrum without the studied sample has been also added to this paper to gain compact imagination (Figure 8-4). In addition of usual impurities of CO2 and H2O, the FTIR spectra also showed the presence of the impurities of CO and surprisingly also HF. In the pure helium discharge the NO and N2O have been detected (Figure 8-4). These compounds could be present due to the possible leaks in the experimental system.

**Figure 8-2:** The infrared absorption spectrum of ICN discharge gaseous products (ICN vapor pressure of 0.75 Torr at room temperature. The broad spectral range is acquired by means of Fourier transform infrared (FTIR) spectroscopy.
The two separate experiments have been performed to study combustion processes (simulated exothermic medium) in hollow cathode and microwave discharge conditions. The tunable diode-laser spectroscopy has been used primarily to investigate the radical cation ICN+ and set of the unknowns lines have been obtained. These lines indicate new species generated by hollow cathode helium discharge with sample of ICN that has been proved by Loomis Wood analyzing software. In addition of impurity of one stronger line at the position 2081.99 cm\(^{-1}\) belongs to the CO molecule, the CN\(^+\) radical has been as well produces in the discharge with the use of ICN and CH3CN as a precursor (this radical plays key role in the studies of such character). Eventually, the high-resolution Fourier transform infrared (FTIR) spectroscopy has been used to get
broad spectral range and individual bands have been identified, especially the fundamental $v_3$ band of main isotopic specie of $^{127}$I$^12$C$^{14}$N molecule that has been proved by published article [37].

**Figure 8-5:** The illustration of the much stronger saturated CO line identification as common impurity from the TDL experiment.
9. Conclusion

The aim of this work is to describe basic principles of the selected spectroscopic methods and to outline their utilization in the field of molecular research in connection to the combustion processes and intermediates of combustion with impact on the environment. The hazardous chemical species in the gas, vapor or aerosol phases constitute serious threat for potentially exposed persons or for living environment. In the case of their abundance in the atmosphere and together with the various adverse factors interactions, these species could cause the extensive losses. With the aid of spectroscopic techniques it is possible to effectively monitor an occurrence of the individual compound or to determine concentrations of partial components in the gas mixture. The spectroscopic methods for detection of the gas phase substances provide rank of valuable information regarding concentration of hazardous chemical compounds in real time and also their spatial propagation. In general, spectroscopic methods are suitable and constantly developing techniques for detection and monitoring of many dangerous molecules, even very low concentration, important from environmental point of view (e.g. the ability to reveal contingency event at the beginning).

10. Related publications


11. Bibliography

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[8] Gordy et. al.


12. Seznam publikací


13. Seznam konferencí


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<th>Radmila Jancěková</th>
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<td>Katedra požární ochrany</td>
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