HIGH-SENSITIVITY DETECTION OF TRACE MOISTURE IN GAS USING CAVITY RING-DOWN SPECTROSCOPY

H. Abe¹, D. Lisak², A. Cygan², R. Ciuryło²

¹ National Metrology Institute of Japan, AIST, Tsukuba 305-8563, Japan
² Institute of Physics, Faculty of Physics, Astronomy, and Informatics, Nicolaus Copernicus University, ul. Grudziadzka 5, 87-100 Torun, Poland

The reliable measurement of residual trace water vapor (trace moisture) in high-purity gases is crucial in the manufacture and design of many cutting-edge products. Various measuring instruments for detecting trace moisture in gases are available commercially and used widely not only at production sites but also in scientific experiments for more than two decades. However, the performance of such instruments in the range below 1 μmol/mol (1 ppm) in amount fraction (mole fraction) has hardly been evaluated experimentally in a manner traceable to the International System of Units (SI) owing to the fact that there was no primary trace-moisture standard until only some years ago.

The National Metrology Institute of Japan (NMIJ) constructed the primary trace-moisture generator in 2007, and using this generator, the performance of some commercially available instruments (two chilled hygrometers and five aluminum oxide capacitive sensors) were tested preliminarily with traceability to the SI. It was found that there are problems with all the instruments in terms of accuracy, time response, and stability (measurement repeatability) in the range below 100 nmol/mol (100 ppb). In contrast, a commercially available trace-moisture analyzer based on cavity ring-down spectroscopy (CRDS) showed an excellent performance in the same range [1]. The noise level (one standard deviation) of the CRDS based trace-moisture analyzer was approximately 0.3 nmol/mol.

In this study, we developed a CRDS based system to improve detection sensitivity for measuring trace moisture in gases. An optical cavity consisting of two highly reflective mirrors (R=0.99994) was used as a sample cell. The standard gas of trace moisture generated using the primary trace-moisture generator was introduced into the sample cell. Laser light with a wavelength of 1.4 μm emitted with a continuous wave laser diode was injected into the sample cell through a mirror on one side of the cell and reflected back and forth inside the sample cell by the highly reflective mirrors. We used the frequency-matched method [2] to couple the laser into the high-finesse cavity. The laser was suddenly turned off after accumulating sufficient power of the light inside the cavity, and the ring-down signals detected with a photodetector placed behind the other side of the mirror were digitized with a 14-bit digitizer. The data were acquired and analyzed using a personal computer. Thanks to its relatively simple experimental setup, this system is quite robust, and therefore, can acquire the data for a long time to improve the detection sensitivity. The tentative analysis of spectra recorded using this system showed that a noise level (one standard deviation) of approximately 10 pmol/mol (10 ppt) was achieved.

GAS TEMPERATURE DETERMINATION IN CO$_2$-CONTAINING DISCHARGES
BASED ON ROTATIONAL SPECTRAL ANALYSIS

Nikolay Britun$^1$, Tiago Silva$^1$, Thomas Godfroid$^2$, Rony Snyders$^{1,2}$

$^1$Chimie des Interactions PlasmaSurface (ChiPS), CIRMAP, Université de Mons, 23 Place du Parc, B-7000 Mons, Belgium,
$^2$Materia Nova Research Center, Parc Initialis, B-7000 Mons, Belgium

The decomposition of CO$_2$, its mixtures, as well as the other greenhouse gases is of a critical importance nowadays. Cold plasma discharges are known to be particularly efficient for this purpose, e.g. those based on the gliding arc, surfatron, or surfaguide microwave discharges, etc. [1,2]. Since the decomposition process normally involves chemical reactions which are sensitive to gas temperature, this quantity has a great importance for understanding the decomposition process. This is also important taking into account the exponential (with gas temperature) character of the vibrational-translational (VT) relaxation in molecular discharges, which in the case of CO$_2$ defines its vibrational modes distribution, and so the decomposition rate [1].

Since in most cases the emission spectra from the diatomic molecules is used for rotational/gas temperature determination, in the case of CO$_2$ discharges only CO or O$_2$ rotational bands may be of use for the mentioned purpose. The essential difference in the decomposition thresholds for these two molecules (11.2 eV for CO vs. 5.2 eV for O$_2$ [3]) makes CO the main candidate for the rotational analysis [2]. In reality, however, due to the presence of nitrogen, water, etc. admixtures in the exhaust gases, N$_2$ and OH rotational bands may also be of interest. This is additionally supported by the fact that both N$_2$ and OH are rather strong emitters in cold plasma discharges.

In this work the experimental results on the gas temperature determination in CO$_2$-containing discharges using the selected rotational emission bands of CO, N$_2$, N$_2^+$, and OH are presented. The results of comparison between the calculated spectra and the experimental ones obtained in our Lab in different discharges under various conditions are analysed. The comparison of the various approaches for rotational/gas temperature determination is undertaken as well. Being acquired under the same experimental conditions, different rotational bands (as well as different methods) show reasonable agreement in terms of the gas temperature values. Finally, since for the practical use the spectra calculation routine as well as its comparison with the experimental results may be time consuming, additional attempts to further simplify the gas temperature determination based on the rotational peak ratio method are undertaken. This way of gas temperature characterization requires only high-resolution spectroscopic measurements following by calculation of the gas temperature by a peak ratio.

INFRARED CROSS-SECTIONS OF NITRO-DERIVATIVES VAPORS: NEW SPECTROSCOPIC SIGNATURES OF EXPLOSIVE TAGGANTS AND DECRADATION PRODUCTS

Arnaud Cuisset¹, Clara Stoeffler¹, Sébastien Gruet², Olivier Pirali²,³, Gaël Mouret¹,

¹Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, 59140 Dunkerque, France
²Synchrotron SOLEIL, L’Orme des Merisiers, St-Aubin BP48, 91192 Gif-sur-Yvette, France
³Institut des Sciences Moléculaires d’Orsay, Université Paris-Sud, 91405 Orsay, France

Classical explosives such as RDX or TNT exhibit a very low vapor pressure at room temperature and their detection in air requires very sensitive techniques with levels usually better than 1 ppb. To overcome this difficulty, it is not the explosive itself which is detected, but another compound more volatile present in the explosive [1]. This volatile compound can exist naturally in the explosive due to the manufacturing process. For example, in the case of DiNitroToluene (DNT), the molecule is a degradation product of TNT and is required for its manufacture. Ortho-Mononitrotoluene (2-NT) and para- mononitrotoluene (4-NT) can be also used as detection taggants for explosive detection.

Using the exceptional properties of the SOLEIL synchrotron source [2], and adapted multipass-cells, gas phase FIR rovibrational spectra of different isomers of mononitrotoluene and dinitrotoluene have been investigated. Room temperature FIR cross-sections of the 3 isomer forms of mononitrotoluene have been determined for the lowest frequency vibrational bands located below 700 cm⁻¹. Both in frequency and in intensity, the harmonic DFT calculations are in good agreement with the FT-FIR measurements. The extension to anharmonic calculations allows simulating some rotational patterns observed in the FIR spectra. Compared to the localized modes at higher frequencies, the THz/FIR vibrational bands give an unambiguous discrimination of the different isomers in a mixture. The weaker volatility of dinitrotoluene required to measure the gas phase FT-FIR spectra at higher temperature (T > 100°C) in flux conditions produced by an evaporating/recondensing system. FIR cross-sections may not be determined, but, compared to a previous gas phase THz study [3], an assignment of active FIR/THz vibrational bands of 2,4-DNT and 2,6-DNT may be performed. Cross sections and their temperature dependences have been measured in the MIR using conventional FTIR spectroscopy probing the nitro-derivatives vapors in a heated multipass-cell.

SYNTHESIS, SPECTROSCOPIC AND THERMAL BEHAVIOR ON SOME BINUCLEAR TRANSITION METAL COMPLEXES OF HYDRAZONES, ANTIMICROBIAL AND CYTOTOXIC STUDIES WITH MOLECULAR ORBITAL CALCULATIONS

Badr A. ElSayed, Salah M. Shaaban

Department of Chemistry, Faculty of Science Al-Azhar University, Nassr City, Cairo, 11844, Egypt

4,6-diacetylresorcinol (DAR)[1] serves as the formation of different hydrazone ligands, which are di, tetra – or hexa – basic with two symmetrical sets of O2N tridentate O2N2 tetradentate or O4N2 hexadentate chelating sites[2]. The condensation of 4,6-diacetylresorcinol and the corresponding hydrazine H6 La and H4 Lb ligands respectively. The structures of these ligands were elucidated by C, H, N elemental analyses, FTIR Fig[1], mass 1H NMR and UV-Vis spectra. Reactions of the hydrazone ligands with Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Cr (III), and Fe (III) ions in 1:2 molar ratios afforded the corresponding transition metal complexes. A variety of binuclear transition metal complexes were obtained in its di-, tetra – or hexa – deprotonated forms. The structure of prepared complexes were identified by elemental analysis, IR, UV-Vis, mass, 1HNMR, magnetic susceptibility measurements and thermal gravimetric analysis TGA. The bonding sites are the azomethine and C=O oxygen atoms in either keto or enol forms and amino nitrogen atoms, and phenolic oxygen atoms. The metal complexes exhibit different geometrical structures such as tetrahedral for [Zn (II) H2Lb] and octahedral arrangements for other metal complexes. The antimicrobial screening of the synthesized compounds H6Lₐ and H4 Lₐ and their complexes were investigated. The Hydrazone ligands showed weaker to significant activity against one or more bacterial and fungal strains. In most of the cases higher activities were exhibited upon coordination with metal ions(II). In addition, calculations in silico, the Pharmacokinetic parameters have promising features for applying the ligands as drugs[3].

MODELLING AND SPECTORSOPIC ANALYSES OF WATER HYACINTH

Medhat IBrahim\(^1\), Hanan Ibrahim\(^2\), Hanan Elhaes\(^3\)

\(^1\)Spectroscopy Department, National Research Center, 12311 Dokki, Cairo, Egypt.
\(^2\)Pollution Research Department, National Research Centre, 12311 Dokki, Cairo, Egypt
\(^3\)Physics Department, Faculty of Women for Arts, Science, and Education, Ain Shams University, 11757 Cairo, Egypt.

Water hyacinth is an aquatic plant which is useful phytoremediation tool. It was divided into root and shoot then analyzed with FTIR, XRF electrical investigations, SEM and molecular modelling. Results indicate that except Sr, CaO, Na\(_2\)O and K\(_2\)O metals and metal oxides are higher in root. FTIR indicated that higher intensities regarded in shoot. Modelling and FTIR indicate that hydrogen bonding of carboxyl group coordinate heavy metals with possible release back to the environment. At room temperature electrical properties of shoot are higher than that obtained for root, which correlated with the type and concentrations of metals.

Water hyacinth could be simulated as 3 cellulose units, one lignin unit and CaO, FeO and Al(OH)\(_3\) respectively. If a structure contains amid group is added to dried plant, the plant could be mediate metals without consuming water and/or oxygen, the proposed material (as seen in figure 1) could be obtained to increase water hyacinth benefits and eliminate its diverse impact. Accordingly self assembly method is utilized to prepare microspheres from dried water hyacinth and chitosan. The analysis of SEM micrograph of obtained microspheres showed that the cellulose structure of water hyacinth is imbedded in the crosslinked chitosan matrix. While FTIR spectrum exhibits only the characteristic bands for raw materials indicating that the formed material is a composite. Batch adsorption kinetic models revealed that the sorption of Pb (II) on microsphere was very fast and the equilibrium was attained within 30 min. The maximum adsorption capacity was 312.5 mg/g, which is about 3 times higher than that of the crude water hyacinth.

Figure 1. Model consists of chitosan, 3 cellulose units linked through O-Linkage with lignin unit. CaO, MgO and Al(OH)\(_3\) are weakly liked through hydrogen bonding with the O-Linkage.
PHOTOACOUSTIC MEASUREMENT OF THE AIR QUALITY WITHIN URBAN POLLUTED SITES

I. R. Ivascu 1,2, C. E. Matei1, M. Patachia1, A. M. Bratu1 and D. C. Dumitras 1,2

1 Department of Lasers, National Institute for Laser, Plasma, and Radiation Physics, 409 Atomistilor St., PO Box MG-36, 077125 Magurele - Bucharest, ROMANIA,

2 Physics Department, Faculty of Applied Sciences, University "Politehnica" of Bucharest, 313 Splaiul Independentei, Bucharest - 060042, ROMANIA

Based on the selective absorption of laser radiation by specific molecules, the photoacoustic spectroscopy technique demonstrated during the years valuable advantages: high accuracy and selectivity being able to measure gas concentrations at sub-ppb levels (partial pressure of $10^{-10}$ atm) [1], non invasive determination, large dynamic range, locally sample and multicomponent capability [2], which recommend it as a powerful technique for pollutant gas trace detection. The measurements are focused on detection of variety of pollutants present in the environmental air such as: ethylene, ethanol, methanol and ammonia. The experimental setup employs a cw tunable frequency stabilized CO$_2$ laser of which discrete spectrum of 53 vibrational-rotational transitions covers the absorption spectra of the interested pollutants within infrared region (9.2 µm ÷ 10.8 µm). Based on the particular absorption spectrum of each target compounds, we analyze the best opportunities to measure the individual gas concentration from the multicomponent mixtures represented by the air samples collected from urban sites with high pollution risk like underground network, boulevards from the city center or a heavy traffic street node. All measurements are performed under atmospheric pressure and room temperature. The minimum detectable concentrations of the individual target compounds in the gas mixture are estimated.

The obtained results are valuable for monitoring of air quality from polluted sites belonging to urban or rural areas, where the presence of such pollutants in the ambient air, even at low level of concentration (ppm range), could affect the people health. By using the CO$_2$ laser as a source in the photoacoustic scheme makes possible detection of various compounds [3], such that this study could be a good premise for accurate measurement of many other air pollutants.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education, CNCS – UEFISCDI, project number PN-II-RU-PD-2012-3 - 0207.

DETERMINATION OF FLUORINE IN TURKISH WINES BY MOLECULAR ABSORBANCE OF CAF USING A HIGH-RESOLUTION CONTINUUM SOURCE ATOMIC ABSORPTION SPECTROMETER

Nil Ozbek, Suleyman Akman

Istanbul Technical University, Faculty of Arts and Sciences, Department of Chemistry, 34469 Maslak, Istanbul, Turkey

Fluorine contents of different types of wines produced in Turkey were determined by the molecular absorption of calcium mono-fluoride (CaF) using a high resolution continuum source graphite furnace atomic absorption spectrometer (HR-CS GFAAS). For this purpose, 2000 µg mL\textsuperscript{-1} of calcium was co-injected to the graphite furnace with diluted wine samples. In order to increase the sensitivities and reduce the LOD and characteristic mass, summation of the absorbances for CaF at 606.440 nm and 606.231 nm were evaluated. Graphite furnace program was optimized and 700°C for pyrolysis and 2250°C for molecule forming temperature is selected for best accuracy. Quantification made by lineer calibration, standard addition technique by HR-CS-AAS and also results compared with ISE method and found no significant difference between each other. The range of F contents for 20 red and white wine samples varies between 0.18 and 0.38. The limit of detection and characteristic mass of the method were 0.18 and 0.058 ng of F, respectively.
A PRACTICAL METHOD FOR THE DETERMINATION OF SULPHUR IN COAL SAMPLES BY HIGH-RESOLUTION CONTINUUM SOURCE FLAME ATOMIC ABSORPTION SPECTROMETRY

A. Baysal¹, S. Akman²

¹ T.C. Istanbul Aydin University, Health Services Vocational School of Higher Education, 34295 Şefakoy Kucukeymece - Istanbul,
² Istanbul Technical University, Faculty of Science & Letters, Department of Chemistry, 34469, Maslak-Istanbul, Turkey

Determination of non-metals (phosphorus, sulphur and the halogens) can be made using line source conventional flame and electrothermal AAS and HR-CS-AAS [1-4]. In this study, sulphur in coal was determined using a high-resolution continuum source flame atomic absorption spectrophotometer (HR-CS-FAAS) with acetylene/air flame. The C–S absorption band at 258.056 nm was found the most suitable analytical line with respect to sensitivity and spectral interferences. The instrumental parameters were optimized. The coal samples were dried and dissolved using microwave-assisted digestion technique. The validity of the method was tested using standard reference material and certified values were found in the limits of 95% confidence level. Since the concentrations of matrix elements of coal other than carbon are low enough not to cause any spectral interferences, the linear calibration method was applied in all quantifications without any problem. The calibration standards were prepared in sulphuric acid. The method was accurate, fast, simple and sensitive. The limit of detection (LOD, 3σ, N = 10) and the limit of quantification (LOQ, 10σ, N = 10) were found to be 0.01 and 0.03% (w/w), respectively. The sulphur concentrations of various kinds of the coal samples received around Turkey were determined. The sulphur contents of the coal samples were ranged from ≤LOQ to 1.2%.