

# **The Plíva Prize Session L**

Lecture Hall AI

**September 1, Thursday, 11:20 – 13:05**

## Towards Precision Infrared Spectroscopy on Small Molecules

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Our goal is a high resolution measurement of the two-photon  $v = 2 \leftarrow v = 0$  vibrational transitions in the hydroxyl (OH) radical with a relative accuracy of  $10^{-14}$ . These transitions can be used for a test of a possible time variation of the electron-proton mass ratio.<sup>1</sup> The core of this endeavor is a laser beam in the mid infrared region at  $2.9 \mu\text{m}$  with a narrow optical linewidth below 1 kHz. This is produced as the idler wavelength of an optical parametric oscillator (OPO) pumped at 1064 nm by a Nd:YAG laser. The same laser is also frequency-doubled and locked to a molecular iodine transition at 532 nm by saturated absorption spectroscopy. By doing this, the Nd:YAG laser obtains a high short term stability, around  $10^{-14}$  at the one-second timescale.<sup>2</sup> To transfer this stability to the idler wavelength of the OPO at  $2.9 \mu\text{m}$ , we make use of an optical frequency comb that spans from roughly 500 nm to 1100 nm. The frequency comb is stabilized to the Nd:YAG laser, and a parasitic output of the OPO at 775 nm, the sum frequency of pump and idler, is compared to the comb. By changing the size of the OPO cavity based on the frequency comb measurement, the idler gets a high short term stability and thus a narrow optical linewidth. The frequency comb is also used to compare the measured absolute frequencies of the various lasers to a GPS-linked radio frequency reference. In this way, we obtain a long-term stability and absolute accuracy for our spectroscopic measurements.

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**Spectroscopic study of Methylglyoxal and its hydrates: a gaseous precursor of secondary organic aerosols**

**August 30 – September 3, 2016, Prague**

**Sabath B. Bteich<sup>1</sup>, Manuel Goubet<sup>1</sup>, Roman A. Motiyenko<sup>1</sup>, Laurent Margulès<sup>1</sup>,  
Thérèse R. Huet<sup>1</sup>**

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Secondary organic aerosols (SOA) have a significant effect on climate change. They are mainly produced in the atmosphere by oxidation of gaseous precursors. Fu et al.<sup>1</sup> have suggested trans-methylglyoxal (MG) as a possible precursor of SOA in the cloud for its presence in large quantities in the atmosphere.

The characterization of SOAs precursors by laboratory spectroscopy allows providing elements for the understanding of the process of formation of these aerosols. For this purpose, we completed the existing pure rotational spectrum of MG in the 12-40 GHz range<sup>2</sup> by new records in a supersonic jet in the 4-20 GHz range (FTMW) and at room temperature in the 150-500 GHz range (mm/sub-mm-wave spectrometer). The analysis was made with the support of quantum chemistry calculations (MP2/CBS and B98/CBS using the Gaussian 09 software). The adjustment of the spectroscopic parameters, taking into account the internal rotation related to the presence of a methyl group, was performed using the RAM36 code. The spectra have been reproduced at the experimental precision up to maximal values of J and K<sub>a</sub> equal to 85 and 35, respectively.

The data obtained for the isolated molecule, both experimentally and theoretically, will allow the study of its hydrated complexes and, by comparison, will give access to (micro-) hydration properties. For this purpose, two stable complexes predicted by theoretical calculations will be studied.

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Type : Talk competes for the PRAHA2016 Plíva Prize.

## Evolutionary algorithm-based analysis of the $\nu_5$ and $\nu_2$ bands of $\text{SOCl}_2$

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Thionyle chloride ( $\text{SOCl}_2$ ) is a volatile inorganic compound extensively used in the industry and whose monitoring in the gas phase is critical both from environmental and military concerns. While the high-resolution ground state microwave spectrum of the main isotopologue  $^{32}\text{S}^{16}\text{O}^{35}\text{Cl}_2$  was recorded some twenty years ago, no further study of the highly spectrally congested spectrum was reported until the pure rotational and rovibrational spectra of  $\text{SOCl}_2$ , and several of its isotopologues, were characterized recently in the microwave, submillimeter, and far-infrared spectral regions<sup>1,2</sup>.

In the present study, the rotationally resolved vibrational spectra of the  $\text{SOCl}_2$  asymmetric  $\nu_5$  ( $459\text{ cm}^{-1}$ ) and symmetric  $\nu_2$  ( $500\text{ cm}^{-1}$ ) stretching fundamental bands have been measured by means of high resolution ( $R = 0.001\text{ cm}^{-1}$ ) FT-FIR spectroscopy on the AILES beamline of the SOLEIL synchrotron facility.

These two bands overlap with a strong  $\text{SO}_2$  band ( $520\text{ cm}^{-1}$ ) arising from the very efficient hydrolysis of  $\text{SOCl}_2$  with residual traces of water<sup>3</sup>.

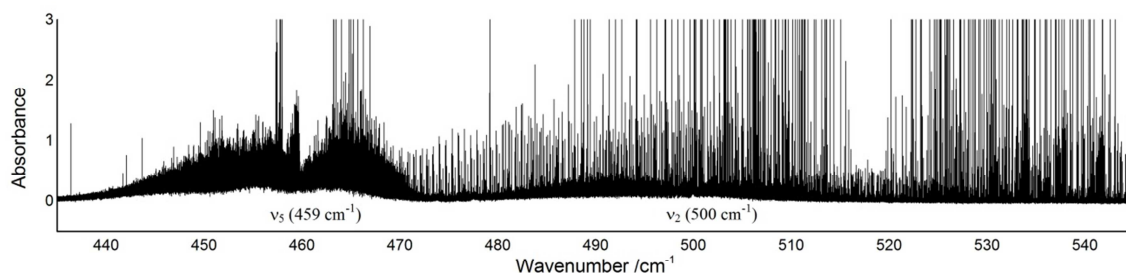


Fig. 1: Spectrum of  $\nu_5$  and  $\nu_2$  bands of  $\text{SOCl}_2$  mixed with a strong  $\text{SO}_2$  band

Evolutionary algorithms implemented in the automated fit programs *ga* and *ga-mr*, developed by the Nijmegen and Düsseldorf groups<sup>4</sup>, have enabled the analysis of the  $\nu_5$  and  $\nu_2$  bands of two isotopologues ( $^{32}\text{S}^{16}\text{O}^{35}\text{Cl}_2$  and  $^{32}\text{S}^{16}\text{O}^{35}\text{Cl}^{37}\text{Cl}$ ), despite the presence of the  $\text{SO}_2$  band and thus demonstrating the power and efficiency of evolutionary algorithms applied to the analysis of congested spectra.

While this analysis yielded the determination of the rotational constants and vibrational band centers, centrifugal distortion constants were obtained from subsequent analysis of the spectrum using traditional spectroscopy methods (Loomis-Wood diagrams).

A global fit containing these new data and all available experimental measurements enabled the determination of accurate molecular parameters (rotational and centrifugal distortion constants, vibrational band centers).

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**Title: Temperature-dependent absorption cross-sections of 3 fluorinated molecules: PFTBA, PFPO, and HFPO**

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We present an overview of temperature-dependent absorption cross sections of 3 fluorinated molecules considered to be greenhouse gases due to being radiatively active in the mid-infrared spectral region. The molecules studied are perfluorotributylamine (PFTBA), 2,2,3,3,3-pentafluoropropanol (PFPO), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFPO). HFPO is a fluorinated liquid commonly used as a speciality solvent for some polar polymers and in organic synthesis. PFTBA and PFPO are commonly used in electronic and industrial applications.

Experimental absorption cross-sections were derived from Fourier transform infrared spectra recorded from 550 to 3400  $\text{cm}^{-1}$  with a resolution of 0.1  $\text{cm}^{-1}$  over a temperature range of 298 to 360 K. These results were compared to theoretical density functional theory (DFT) calculations and previously published experimental measurements made at room temperature<sup>1,2,3,4</sup>.

Theoretical DFT calculations were performed using the B3LYP method and the 6-311G(d,p) basis set. The calculations have determined the optimized geometrical configuration and infrared intensities and wavenumbers of the harmonic frequencies for different ground state configurations due to the presence of internal rotors. We used the energies of these configurations to the population of each configuration as a function of temperature using a Boltzmann distribution to predict how the experimental spectra will respond to temperature.

Furthermore, we calculated the radiative efficiencies and the global warming potentials and compared them to previously published values<sup>5</sup>.

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## Infrared spectroscopic investigation of nuclear spin conversion of methane in a xenon matrix

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Methane exists in three kinds of nuclear spin isomers: para ( $I = 0$ ), ortho ( $I = 1$ ), and meta ( $I = 2$ ). Each isomer is related to the particular rotational states because the total molecular wave function must be antisymmetric under exchange of two protons. The nuclear spin conversion of methane in various condensed systems has been studied both theoretically and experimentally.<sup>1-4</sup> According to the theoretical studies,<sup>1,2</sup> the surplus rotational energy emitted during nuclear spin conversion is transferred to phonons of a surrounding medium. Thus, the rate of the nuclear spin conversion,  $k$ , depends on the matrix species. In the present study, we investigated the nuclear spin conversion of methane in a xenon matrix at the temperatures of 6.0-12.0 K in order to compare it with that in argon, krypton, and para-hydrogen matrices and solid methane.<sup>2-4</sup>

Our experimental apparatus is composed of a vacuum chamber equipped with a liquid helium flow cryostat, an infrared spectrometer, and a HgCdTe detector. The sample was prepared by spraying the premixed gas with the mix ratio of  $\text{CH}_4/\text{Xe} = 0.05 \pm 0.02\%$  on a gold substrate. Spectral measurements were conducted at the resolution of  $1.0 \text{ cm}^{-1}$  in the reflection configuration with the incident angle of 80 degrees.

Figure 1 shows infrared spectra of methane in a xenon matrix just after and about 2 hours after annealing at 55 K. Several  $\nu_4$  rovibrational peaks are observed. The absorption peak due to the R(0) branch increases and those due to P(1), Q(1), and R(1) decrease in intensity. This temporal change corresponds to the rotational relaxation associated with the nuclear spin conversion of  $I = 2 \leftarrow 1$ . From analyses of the temporal changes of the peak intensities, we obtained the conversion rate,  $k = 1.35 \pm 0.06 \text{ h}^{-1}$ , at 6.0 K. The  $k$  values were determined in the temperature range of 6.0-12.0 K and the temperature dependence was analyzed in terms of the combination of the single phonon process and thermally activated one.<sup>4</sup> In addition, it was found that the shifts of the rovibrational peaks from the gas phase frequencies depend on the matrix species. We will discuss the shifts on the assumption of the Lennard-Jones potential between methane and neighboring matrix molecules.

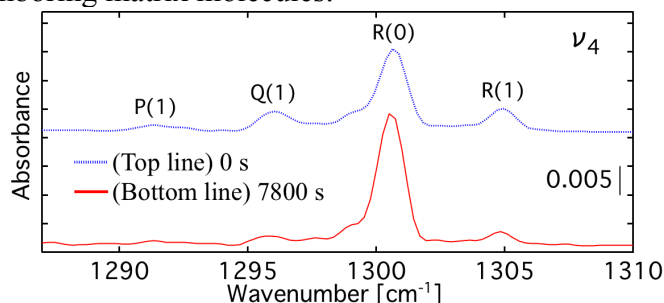


Fig. 1: Infrared spectra of methane in a xenon matrix at 6.0 K.

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## High-level theoretical rovibrational spectroscopy of linear triatomic molecules

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A near equilibrium potential energy surfaces (PES) for the thioformyl cation  $\text{HCS}^+$  ( $X^1\Sigma^+$ ) is employed in variational calculations for many rovibrational states. The PES is constructed in a high-level composite approach that combines explicitly correlated coupled cluster theory with corrections due to inner shell correlation, scalar relativistic effects and higher-order correlation up to pentuple excitations. Effects beyond the Born-Oppenheimer approximation are accounted for by the diagonal Born-Oppenheimer correction (DBOC). It will be shown that this level of *ab initio* calculations allows to reliably obtain accurate molecular geometries, vibrational band origins to within  $1\text{ cm}^{-1}$  and rotational constants within 0.01 % of experiment<sup>1</sup>. Comparisons with isoelectronic species like  $\text{HCO}^+$ ,  $\text{HCN}$  and  $\text{HCP}$  are made. The overall performance shows that the applied approach consistently provides close to perfect agreement with experiment, allowing for the elucidation of spectral features such as anharmonic couplings between rovibrational states<sup>1,2</sup>, local perturbations<sup>1</sup> and intensities of rovibrational transitions<sup>3</sup>.

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## Vibrational Spectroscopy of Small Silicon-Carbides

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Silicon-carbides, e.g., SiC, SiC<sub>2</sub>, Si<sub>2</sub>C, c-SiC<sub>3</sub>, and SiC<sub>4</sub>, have been found in circumstellar envelopes by means of radio-astronomical observations. They are thought as building blocks of interstellar dust grains featuring the characteristic infrared emission at 11.5  $\mu\text{m}$  in cool evolved carbon-rich giant stars.

Despite their prominent role in astrochemical processes of dust formation the laboratory spectroscopy of silicon-carbides is still in its infancy and rotationally resolved spectra are rather sparse. In view of a new generation of high resolution infrared telescope instruments, e.g., the Echelon-Cross-Echelle Spectrograph (*EXES*) onboard SOFIA (Observatory for Infrared Astronomy), accurate laboratory data of small silicon-carbides are of high demand.

We present a general technique to produce gas phase molecules of refractory elements in a supersonic jet. A pulsed Nd:YAG-laser is used to vaporize a solid target of silicon exposed to a dilute sample of methane in helium buffer gas. Small silicon-carbides are formed in a free jet expansion and are subsequently cooled by adiabatic expansion into a vacuum chamber. Radiation of quantum cascade lasers at wavelengths of 8-11  $\mu\text{m}$  are used to record rotationally resolved spectra of small silicon-carbide molecules. The high resolution spectra give insights to their molecular structure, the ro-vibrational dynamics and characteristic spectral features for future astrophysical detections.