

SIMULTANEOUS ABSORPTIVE AND DISPERSIVE MEASUREMENTS WITH CAVITY-ENHANCED SPECTROSCOPY

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Our recent results on quantitative comparison of three precise cavity-enhanced techniques of molecular spectra collecting are presented. The first one, based on the determination of photon lifetime in the cavity, is well established frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) [1-3]. The second method is an improved version of cavity mode-width spectroscopy (CMWS) [4,5]. The third technique is based on the measurements of the cavity free spectral range, which changes in presence of a molecular transition. The first two techniques measure the absorption of the sample, while the third one its dispersion.

A comparison of shapes of particular molecular transitions measured with three independent techniques will allow for estimation of upper limits of the systematic errors introduced by these methods. Such comparison is of great importance for the line-shape analysis of experimental spectra, where one of the most challenging task is to distinguish the systematic error coming from experimental imperfections from these caused by the wrong choice of the line-shape model, see e.g. [6].

CRDS and CMWS techniques are complementary, in the sense that they achieve their best precision in different pressure ranges. For low absorptions the best precision is achieved with the CRDS technique, where the ring-down times are long and hence they can be well determined. In the opposite case, where the absorption is high, the precision of CMWS is enhanced [5]. The third method, based on the measurement of radio frequency seems to be insensitive to nonlinearity in detection system of the cavity transmission signal.

We tested these three methods on the CO rovibrational transitions from the (3←0) band around 6201 cm⁻¹.

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**INELASTIC COLLISIONS IN O₂+He SUPERSONIC JETS BY
HIGH-RESOLUTION RAMAN SPECTROSCOPY**

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High-resolution Raman spectroscopy has been employed to study the O₂:He inelastic collisions at temperatures from 10 to 40 K. For that purpose, a number of supersonic microjets of O₂:He mixtures free from O₂ condensation, with O₂ mole fractions ranging from 0.025 to 0.50, have been quantitatively characterized in terms of number densities $n(z)$ and rotational populations $P_J(z)$ along the jet direction (z) by means of the rotational and vibrational Raman spectra. Number densities $n(z)$ were obtained by comparing the intensity of the fundamental Q-branch at 1555 cm⁻¹ in the jet with that from a static sample at a known number density, while rotational populations are extracted from the integrated intensities of the triplets associated with the $N \rightarrow N+2$ Raman transitions, N being the rotational angular momentum [1].

These primary data are reduced to rotational $T_{\text{ROT}}(z)$ and translational $T_{\text{TRA}}(z)$ temperatures. Translational temperatures have been obtained from number densities and rotational temperatures by conservation of mass, momentum, and enthalpy along the jet [2]. These measurements can be linked to calculations of state-to-state rate coefficients by means of the kinetic Master Equation, which accounts for the time evolution of the rotational populations. The rate coefficients have been computed [3] by solving the close-coupling equations for O₂ + He collisions and using an accurate *ab initio* potential energy surface [4]. A careful analysis of the Master Equation, which combines experimental and theoretical data, allows us to assess the accuracy of the rate coefficients and, in turn, of the potential energy surface.

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H₂O NUCLEAR-SPIN CONSERVATION/RELAXATION IN SUPERSONIC JET EXPANSION PROBED BY QUANTITATIVE DIRECT ABSORPTION SPECTROSCOPIC DETECTION

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Molecular species with several identical nuclei with non-zero nuclear spins generally exist in several distinct isomers that differ by the total value of nuclear angular momentum. Transitions between those nuclear-spin isomers represent an important fundamental physical process and have been studied since the discovery of ortho/para H₂ early in the 20th century. In general, transitions between different nuclear-spin isomers proceed with very low probabilities in the gas phase for both radiative and collisional processes. As a result, it has been shown for a wide range of species that nuclear-spin is conserved during supersonic jet expansion, where the gas temperature is rapidly lowered from room temperature to few K on the time scale of several micro seconds. Recent report by Manka Tanner, Quack, and Schmidiger [1] however indicate that rapid nuclear-spin isomerization takes place in supersonic jet expansion of H₂O. This unexpected observation has been correlated with cluster formation in the expanding gas. This nuclear-spin relaxation in clustering molecular beam has been rationalized by possible rapid isomerization inside the clusters and fast exchange of H₂O molecules between the clusters and gas-phase monomers in the expansion. However at this point no theoretical justification of such process is available and independent experimental data are limited.

In the presented contribution we re-investigate in detail the nuclear-spin conservation/relaxation processes during the supersonic cooling of H₂O in Ar expansions using the Prague Slit-Jet-NIR-LAS spectrometer [2]. We use high resolution direct absorption spectroscopic detection in the first OH overtone region near 7200cm⁻¹ to quantitatively measure the temperatures as well as the quantum state specific concentrations of various H₂O rotational states in the expanding gas. We specifically sample concentrations of the lowest rotational states for para (0₀₀) and ortho (1₀₁) nuclear-spin isomers respectively. Depending on the H₂O fractional concentration and total stagnation pressure the supersonic expansion temperature and level of cluster formation are controlled. The experimentally determined population ratios for the para/ortho nuclear-spin isomers are compared to theoretical predictions assuming both nuclear-spin conservation and relaxation cases.

The preliminary data indicate that under the conditions of our experiment we do not observe any correlation between clustering in the expansion and nuclear-spin isomerization. Our data are within the experimental error consistent with the nuclear-spin conservation during the supersonic cooling. It is estimated that for all the investigated expansion conditions less than 20% relaxation is observed.

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REINVESTIGATION OF THE FIRST TORSIONAL BAND OF METHYLAMINE

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Methylamine, CH₃-NH₂, is the simplest primary amine performing two large amplitude motions: hindered internal rotation of the methyl (CH₃) group about the C-N bond and inversion of the amino group (NH₂). These two large amplitude motions are strongly coupled and give rise to a fine structure in the vibrational states. The rovibrational spectrum of the methylamine molecule has been extensively studied both experimentally and theoretically. Previously, the far-infrared spectrum of CH₃NH₂ in the region of 40-350 cm⁻¹ with resolution of 0.005 cm⁻¹ has been analyzed by N. Ohashi et al. [1].

We present the restudy of the first torsional band of methylamine in the 40-360 cm⁻¹ region with a resolution of 0.00125 cm⁻¹. Over 7500 transitions with $0 \leq K \leq 20$ and $K \leq J \leq 40$ have been assigned what is a major improvement comparing to the previous study. A global fit has been carried out based on a group theoretical formalism [2].

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MICROWAVE AND INFRARED SPECTROSCOPIES OF α - AND β -PINENE
COMPLEMENTED BY QUANTUM CHEMICAL CALCULATIONS

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Several monoterpenes are biogenic volatile organic compounds (BVOCS) present in the atmosphere. They can react with OH, O₃, NO_x, etc. to give rise to several oxydation and degradation products. We have studied the gas phase spectroscopy of two bicyclic atmospheric monoterpenes, the α - and β -pinene (C₁₀H₁₆). In the first step of this work, quantum chemical calculations and microwave spectroscopy were used in order to evidence the stable conformers, using a well-established methodology [1-2]. In a second step infrared spectra have been recorded on the FTIR spectrometer of the AILES beamline at synchrotron SOLEIL, using the Jet-AILES molecular beam and a long path cell. Special attention was paid to the 700–1300 cm⁻¹ atmospheric window, to the CH vibration region, and to the fingerprint FIR region. Quantum chemical calculations have been performed at different levels of theory (DFT, *ab initio*). In particular anharmonic force fields were obtained in order to model the vibrational structures.

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QUANTUM MONODROMY IN NCNCS: TOWARDS A FULLY EXPERIMENTAL ENERGY-MOMENTUM MAP OF THE LARGE-AMPLITUDE BENDING MODE

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The NCNCS molecule is bent in its ground state, with a low-frequency (85 cm^{-1}) in-plane bending mode. The potential energy function governing the bending motion is two-dimensional, and is shaped like the bottom of a champagne bottle. In NCNCS, the barrier to linearity (the top of the hump in the potential function) is at 285 cm^{-1} , well below the next fundamental vibration at about 430 cm^{-1} . These properties make NCNCS ideal for studies of the physics of quantum monodromy, which manifests itself as a dislocation of the pattern of energy levels in an energy-momentum map as the molecule's energy crosses over the barrier to linearity.

We present the results of extensive spectroscopy of NCNCS conducted at both The Ohio State University[1], where pure rotational data were collected with the FASSST THz spectrometer, and at the Canadian Light Source in Saskatoon, SK, where extensive rotation-vibration spectra were obtained at high resolution using synchrotron radiation as background radiation for absorption measurements[2]. We will provide an update on our current efforts to create a fully-experimental energy-momentum map for the bending mode of NCNCS using both the rotational and rotation-vibration data, and on the results of fitting our data using the Generalized Semi-Rigid Bender Hamiltonian, which can properly account for the large-amplitude bending motion.

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