# MO 23: Progress on Various Topics in Molecular Physics

Time: Friday 11:00–12:45 Location: PH/SR106

MO 23.1 Fri 11:00 PH/SR106

**Torsion and Bending Motion of $^{13}$C Substituted Dimethyl Ether** — •Pia Kutzer[1], Olivier Pirali[2], Pascale Roy[2], and Thomas Giesen[1] — [1]Universität Kassel, Institut für Physik, Heinrich-Plett Str. 40, D-34132 — [2]Sociètè civile Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48, F-91192 Gif Sur Yvette Cedex

Dimethyl ether (DME) shows large amplitude internal motion. The internal torsion of both methyl groups exhibits strong coupling effects of the rotors and with the C-O-C in plane bending mode.

The molecule is well-studied by means of high resolution spectroscopy, although there are still some important open questions left, especially in case of the $^{13}$C substituted species. Calculated band centre frequencies of the torsional motion obtained from high level *ab initio* calculations still deviate from experimental values, and comparison to $^{13}$C substituted species was so far restricted to few measurements of pure rotational transitions.

Recently, we recorded first high resolution broadband spectra of singly and doubly $^{13}$C substituted DME using a FT-IR spectrometer at SOLEIL synchrotron laboratories. We also recorded spectra of these species at Kassel at a lower resolution.

Here we present our ongoing analysis of the C-O-C bending mode of the three isotopologues and preliminary results for the first torsionally excited states.

Our measurements and analyses will help to foster quantum chemical modelling of large amplitude motion.

MO 23.2 Fri 11:15 PH/SR106

**Investigation of ETFE Plastic Foils Using Raman Spectroscopy and Chemometric Analysis** — •Alexandru Popa, Rasha Hassanein, and Arnulf Materny — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

Ethylene-tetra-fluoro-ethylene (ETFE) is a fluorine-based plastic, which presents excellent thermal and mechanical properties such as durability, flexibility, as well as light-weight, low frictional coefficient, long-term stability against solar degradation, and transmissivity of all visible wavelengths. Due to these outstanding characteristics, ETFE foils have become more and more popular in building applications, as roofing. Within the current contribution, ETFE samples produced by two manufacturers and with coatings applied by different companies have been investigated using confocal micro Raman spectroscopy with 514.5nm excitation. The confocal setup allowed for high depth resolution required to access the interface between coating and ETFE foil. The aim of the study was the comparison of print quality from two manufacturers for different ink types, as well as the correlation of print quality to the adhesion of the ink onto the surface of the foil. Samples were obtained and Raman spectroscopically investigated at different time-steps: after the coating took place and at different times while they were exposed to an accelerated weathering system with UV radiation, heat, and humidity. Changes seen in the Raman spectra will be discussed.

MO 23.3 Fri 11:30 PH/SR106

**Tuning the non-radiative lifetime of molecular aggregates via the dipole-dipole interaction** — •Alan Celestino and Alexander Eisfeld — MPIPKS, Dresden, Germany

Non-radiative transitions lead in many molecules to a relaxation from the electronic excited to the ground state on a time scale faster than that of spontaneous emission. Therefore the excitonic lifetime in those molecules is limited by their non-radiative transition channels. Depending on the application in mind one would like to tune these lifetimes (making them longer or shorter). Here we show that aggregation of such molecules strongly influences the non-radiative lifetime. By varying the dipole-dipole interaction between the molecules one can either enhance the the non-radiative lifetime or even totally suppress it. We study in detail a molecular dimer. The monomer is modeled as a two electronic level system coupled to a single nuclear coordinate (relevant nuclear coordinate). The remaining nuclear coordinates are taken into account as a Markovian bath coupled to the relevant nuclear coordinate. The two electronic potential surfaces are coupled via a non-radiative well-localized exciton-decay channel. The dimer is composed by two dipole-dipole-interacting monomers. The dipole-dipole interaction leads to completely new dynamics and allows one to tune the excitonic lifetime.

MO 23.4 Fri 11:45 PH/SR106

**Matrix Completion: Enhancing the Measurement Efficiency in 2D Spectroscopy** — •Matthias Kost — Department of Theoretical Physics, Ulm University, Germany

2D spectroscopy is an indispensable tool in various modern sciences like physics, biology, chemistry and medicine. In particular, it resolves useful information about the inner electronic and spatial structure of molecules in a sample. However, the gain of high resolution requires a large number of measurements, which is one of the central problems concerning measurement efficiency.

Matrix completion is a mathematical procedure, providing the ability to recover certain matrices from just a few of its entries. This talk demonstrates, how the application of such algorithms in the context of 2D spectroscopy leads to significantly less measurement effort. This enhancement may be a crucial step towards the feasibility of more complex 2D spectroscopy methods.

MO 23.5 Fri 12:00 PH/SR106

**The Bending Vibration of the $C_3$-Molecule and its Isotopologues in the Terahertz Region** — •Thomas Büchling, Alexander Breier, Guido Fuchs, and Thomas Giesen — Universität Kassel, Institut für Physik, Heinrich-Plett Str. 40, 34132 Kassel

Short carbon chains are fundamental for the chemistry of stellar and interstellar ambiences: They are omnipresent throughout the interstellar medium, they likely participate in the formation of long carbon chains and they are products in photo-fragmentation processes of larger species.

Triatomic carbon $C_3$ exhibts a mid-infrared $\nu_3$ antisymmetric streching mode and a $\nu_2$ bending vibration at 1.9 THz. The detection of $\nu_2$ is experimentically challenging as radiation sources in the terahertz frequency region were missing for a long time as they are in the transition area between optical and microwave techniques.

In our experiment carbon is vaporized by laser-ablation and diluted in a supersonic jet of helium. Through absorption spectroscopy the molecular constants of the main isotopologue $^{12}C^{12}C^{12}C$ and of singly $^{13}$C substituted species are derived.

These laboratory measurements are taken as a basis for further astrophysical observations of different $C_3$-isotopologues. This will lead to a better understanding of the chemistry of the stellar and interstellar medium.

MO 23.6 Fri 12:15 PH/SR106

**Diffractive imaging of dissociating molecules using X-ray free-electron lasers** — •Fenglin Wang[1,2], Stephan Stern[1], Henry N. Chapman[1,3,4], and Jochen Küpper[1,3,4] — [1]Center for Free-Electron Laser Science (CFEL), DESY, 22607 Hamburg, Germany — [2]PULSE Institute, Stanford University, Stanford, California 94305, USA — [3]Department of Physics, University of Hamburg, Luruper Chaussee 149, 22671 Hamburg, Germany — [4]Center for Ultrafast Imaging (CUI), University of Hamburg, 22607 Hamburg, Germany

Free-electron lasers (FELs) can provide very intense, ultrashort pulses of coherent X-rays. This allows for diffractive techniques to see single molecules at spatially and temporally atomic resolution (pm and fs). We use ensembles of laser-aligned isolated molecules to demonstrate these imaging techniques with FELs and to record “molecular movies” of structural dynamics in a bottom-up approach. Here, we present a holographic idea that allows to disentangle the multiple simultaneously pathways occurring in the photodissociation of complex molecules. In this *fragmentation holography* the incoherent contributions from different pathways are directly separable in the Fourier transform of the diffraction patterns. This will enable us to gain access to structural information of fragmenting molecules as a function of pathways and time.

MO 23.7 Fri 12:30 PH/SR106

**Relativistic Density Functional Calculations of Chemical Shifts of Manganese K X Rays** — Burkhard Fricke[1], •Khalid Rashid[2], and Detlev Gotta[3] — [1]Institut für Physik, Universität Kassel,Germany — [2]National University of Science and Technology,

Islamabad, Pakistan — [3]Institut für Kernphysik, Forschungszentrum Jülich, Germany

The complexity of the origin of the K energy shifts arising from the electronic structure of 3d electrons in the Liegand field of the compound makes the interpretation a formidable problem. Here a theoretical attempt is made to understand the K energy shifts of Mn atom coming from different chemical environment measured by D. Gotta et. al. Relativistic density functional theory calculations are made with the CLUSTER code developed at Kassel University. The chemical environment of the Mn compound is simulated by a model cluster of six closest neighbour atoms placed on a grid. Vectors of the neighbour atoms are extracted from the available data of electronic structure of Mn compounds. The K$\alpha$1 and K $\alpha$2 line energies are determined by calculating the total energies of the complex of manganese and its six neighbour atoms for 1s, 2p1/2, and 2p3/2 hole states and building their differences. Calculated K shifts for K $\alpha$2 are of the same order of magnitude as the measured shifts except for the MnF3 case. For K$\alpha$1 shifts however the spread between theory and experiment is relatively larger.