

MO 19: Electronic Spectroscopy

Time: Thursday 14:30–16:15

Location: PH/HS1

Invited Talk

MO 19.1 Thu 14:30 PH/HS1

Luminescence properties of mass-selected lanthanoid complexes: a study involving gas-phase ion trapping, ion deposition into neon matrices, and computations. — ●JEAN-FRANCOIS GREISCH¹, BASTIAN KERN², MICHAEL E. HARDING¹, JIŘÍ ČHMELA², BERNHARD SCHÄFER¹, ARTUR BÖTTCHER², WIM KLOPPER^{1,2}, MARIO RUBEN^{1,3}, DETLEF SCHOOSS^{1,2}, DMITRY STRELNIKOV², PATRICK WEIS², and MANFRED M. KAPPES^{1,2} — ¹Inst. of Nanotechnology, KIT (D) — ²Inst. of Physical Chemistry, KIT (D) — ³Inst. de Physique et Chimie des Matériaux, CNRS-Uni. Strasbourg (F)

Charged lanthanoid-antenna complexes are relevant to many fields, e.g., photovoltaics, light-emitting diodes, and quantum memories. Investigation of their excited state properties directly benefits from mass spectrometric methods since their luminescence is strongly affected by stoichiometry, symmetry, and overall charge state. The talk focuses on a comparison between the luminescence properties of mass-selected ions (i) isolated in solid cryogenic neon matrices and (ii) in a Paul trap. For series of complexes having common stoichiometry but varied lanthanoid composition we observe vibrationally-resolved ligand-centered or lanthanoid-centered emission. Energy level shifts and splittings are rationalized in terms of structural changes, which were analyzed with the support of ion mobility measurements. The role of the ligand shell and the induced ligand field on the lanthanoid's energy levels, as well as the differences in the vibrationally resolved spectra, are interpreted with the support of density functional theory combined with Judd-Ofelt theory and Franck-Condon computations, respectively.

MO 19.2 Thu 15:00 PH/HS1

Exciton coupling in [AB](N) copolymers — ●KLAUS RENZIEHAUSEN¹, CHRISTOPH LAMBERT², and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Universität Würzburg, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Center for Nanosystems Chemistry, Am Hubland, 97074, Würzburg, Germany

In order to understand basic optical properties of alternating copolymers we use exciton coupling theory in which the excited states of the polymers are generated by coupling of localized excited states of the monomers A and B. The mathematical description of the copolymers follows essentially the work of Kasha [1]. Within this model it is possible to explain the absorption lineshape of a squaraine-squaraine copolymer which was measured recently [2].

[1] Kasha, M. *Radiat. Res.* 20, 55-71 (1963)

[2] S. F. Völker, A. Schmiedel, M. Holzappel, K. Renziehausen, V. Engel, Ch. Lambert *J. Phys. Chem. C* 118, 17467 (2014).

MO 19.3 Thu 15:15 PH/HS1

Geometry changes of ortho- and meta-Tolunitrile upon S1 -> S0 excitation: comparison of the effect of substituent positions in push-pull systems — ●FELIX GMEREK and MICHAEL SCHMITT — Heinrich-Heine-Universität, Düsseldorf, Germany

The nuclear structure of a molecule follows its electronic structure in the specific electronic state. Therefore, it is strongly influenced by electron pushing or pulling substituents and can easily be investigated by electronic spectroscopy.

Tolunitriles represent small push-pull-systems with an electron-pushing methyl-group and an electron-pulling cyano-group.

In this project, the ortho- and meta-isomers were investigated to compare the effects of different substituent positions.

According to the Franck-Condon-principle the fluorescence intensities depend on the geometry changes. Therefore the excited state geometry can be described by a displacement of the ground state, which is derived from the Franck-Condon-factors and the rotational constant changes.

The rotational constant changes upon electronic excitation have been measured by Alvarez-Valtierra et al. [1]. Additionally Franck-Condon-factors were obtained by single vibronic level fluorescence spectroscopy of the electronic origin and six vibronic bands for both isomers.

[1] personal communication

MO 19.4 Thu 15:30 PH/HS1

Non-Adiabatic Relaxation of Multi-Electronic Dynamics in Polycyclic Aromatic Hydrocarbons — ●MARTIN GALBRAITH¹,

THOMAS BARILLOT², VICTOR DESPRE², JESSE KLEI¹, ALEXANDER KULEFF³, VINCENT LORIOU², SUSANTA MAHAPATRA⁴, ALEXANDRE MARCINIAK², JOCHEN MIKOSCH¹, SAMALA NAGAPRASAD REDDY⁴, ARNAUD ROUZEE¹, CHRISTOPHER SMEENK¹, ALEXANDER TIELENS⁵, CHUNG-HSIN YANG¹, NICKOLAI ZHAVORONKOV¹, MARC VRACKING¹, and FRANCK LEPINE² — ¹Max-Born-Institut, Berlin, Germany — ²Institut Lumiere Matiere, Universite Lyon 1, Villeurbanne Cedex, France — ³Universitaet Heidelberg, Heidelberg, Germany — ⁴University of Hyderabad, Hyderabad, India — ⁵Leiden University, Leiden, The Netherlands

We present experimental evidence for an ultrafast relaxation mechanism that follows absorption of an XUV photon and is general for polycyclic aromatic hydrocarbons (PAH). Highly excited electronic states are created where electron correlation effects play a dominant role. The excitation of shake-up states by ionisation is followed by non-adiabatic relaxation dynamics on a time scale of 10s of fs. Various PAHs and their building block benzene have been studied with XUV pulses from high-harmonic generation and an infrared probe pulse, leading to a time resolution down to sub-10 fs. The XUV-induced photochemistry of PAHs is of great interest in astrophysics due to their long-debated role in the origin of the diffuse interstellar bands. The satellite states in PAHs make these molecules interesting candidates for investigating attosecond hole migration following ionisation.

MO 19.5 Thu 15:45 PH/HS1

Determination of excited state dipole moments of various indole derivatives using rotationally resolved laser induced fluorescence spectroscopy — ●MARTIN WILKE¹, JOSEFIN WILKE¹, MICHAEL SCHMITT¹, and LEO MEERTS² — ¹Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf — ²Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

In solution the energetic order of the lowest excited singlet states of indole, called La and Lb in the nomenclature of Platt, depends dramatically on the polarity of the surrounding solvent. For the gas phase it could be shown that the energetic order can be influenced and even inverted by the insertion of differently acting substituents to the indole chromophore. High resolution laser induced fluorescence spectroscopy can be used to assign the electronic nature of excited singlet states from the orientation of the transition dipole moment or the magnitude of the permanent dipole moment of the electronically excited state. Therefore a homogeneous static electric field is created, which lifts the M degeneracy by the Stark effect and results in a band splitting depending on the intensity of the electric field and on the order of the dipole moment in the ground and in the excited state. The Stark spectra of several indole derivatives have been measured and analyzed using an evolutionary algorithm. Thereby the nature of the excited state can be discussed by means of its dipole moments.

MO 19.6 Thu 16:00 PH/HS1

Single Molecule Magnets investigated by gas phase X-ray Magnetic Circular Dichroism (XMCD) spectroscopy — ●MATTHIAS TOMBERS¹, JOACHIM HEWER¹, JONATHAN MEYER¹, GEREON NIEDNER-SCHATTEBURG¹, and TOBIAS LAU² — ¹Fachbereich Chemie & Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Kaiserslautern, Germany — ²Helmholtz-Zentrum Berlin für Materialien und Energie, BESSY II, Berlin, Germany

We have recorded the first XMCD spectra of different isolated Single Molecule Magnets (SMMs) in the gas phase to deduce their intrinsic magnetic properties void of any surface or packing effects. We report the XMCD spectrum of the archetypal SMM Mn12-acetate on the Mn L3,2 absorption edges. Furthermore, we recorded the XMCD spectra of different [Fe4Ln2Lx]-type SMMs (Ln=Gd, Tb, Dy; L = different organic ligands) on the Fe L3,2- and the Ln M5,4- absorption edges respectively. The element selectivity of the XMCD technique allows us to determine the contribution of the different metals to the total magnetic moment of the molecules. Furthermore, sum rule analysis of the recorded XMCD spectra allows us to separate the total magnetic moment into its spin and orbital contribution. We have performed InfraRed Multi Photon Dissociation (IRMPD) spectroscopy of these molecules to address those magnetic moments to their structural features.