

## MO 23: Electronic Spectroscopy II

Time: Thursday 14:30–16:00

Location: MER 02

**Invited Talk**

MO 23.1 Thu 14:30 MER 02

**Eigenstate resolving molecular spectroscopy in the gas-phase: towards larger systems and higher energies** — ●MICHAEL SCHMITT<sup>1</sup>, CHRISTIAN BRAND<sup>1</sup>, OLIVIA OELTERMANN<sup>1</sup>, and LEO MEERTS<sup>2</sup> — <sup>1</sup>Heinrich Heine Universität, Düsseldorf, Deutschland — <sup>2</sup>Radboud University, Nijmegen, The Netherlands

Intrinsic properties of large isolated molecules can be investigated by eigenstate resolving electronic spectroscopy. The rotationally resolved spectra even of medium sized flexible molecules are generally quite congested due to the existence of various conformers, which often spectrally overlap. The spectral discrimination of conformers by their center frequency due to different zero-point energies or electronic effects is one of the most important benefits of this method compared to other, higher resolving techniques like microwave spectroscopy. Direct evaluation of the molecular parameters using line position assigned fits are in most cases difficult or impossible. Automated fits without the need for manual quantum number assignments using Genetic or Evolutionary Algorithms have been shown to be very successful in these cases.

Information about vibronic coupling between higher vibronic states is contained in the intensities of individual rovibronic transitions and can be used for a more thorough understanding of photophysical processes at high energies. Applications of the method in order to unravel the mystery why properties of electronically excited states of some flexible molecules are extremely sensitive to the conformation, while others are not, will be given. The limitations and prospects of the method will be discussed.

MO 23.2 Thu 15:00 MER 02

**Probing dissociative molecular dications by mapping of vibrational wavefunctions** — ●RALPH PÜTTNER<sup>1</sup>, TIBERIU ARION<sup>2</sup>, MARKO FÖRSTEL<sup>2,3</sup>, TORALF LISCHKE<sup>2</sup>, MELANIE MUCKE<sup>2</sup>, VLADIMIR SEKUSHIN<sup>1</sup>, GÜNTER KAINDL<sup>1</sup>, ALEXANDER BRADSHAW<sup>2,4</sup>, and UWE HERGENHAHN<sup>2</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Germany — <sup>2</sup>Max-Planck-Institut für Plasmaphysik c/o Helmholtz-Zentrum Berlin, Germany — <sup>3</sup>Max-Planck-Institut für Kernphysik, Heidelberg, Germany — <sup>4</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We present high-resolution photoelectron-Auger electron coincidence spectra of CH<sub>4</sub>. Since the vibrational structure in the C 1s photoelectron spectrum is resolved, Auger spectra corresponding to the vibrational levels  $v = 0$  and 1 can be extracted. These spectra display pronounced differences due to the fact that the energy spectrum of a transition to a dissociative state reflects the squares of the vibrational wavefunction,  $\Psi_{vib}(Q)$ , in the core-ionized state. By implementing this in a simultaneous fit of both spectra we have separated the Auger transitions to all 7 states of dicationic CH<sub>4</sub><sup>2+</sup> present in this energy region. We were able to derive the energy values and slopes of the potential energy curves of the dicationic states and have found good agreement with other experimental and theoretical results.

MO 23.3 Thu 15:15 MER 02

**Electronic structure of pyrimidine bases** — ●THOMAS SCHULTZ<sup>1</sup>, KYRIAKI KOSMA<sup>2</sup>, CHRISTIAN SCHRÖTER<sup>1</sup>, and HANS-HERRMAN RITZE<sup>1</sup> — <sup>1</sup>Max Born Institut, Max-Born Strasse 2A, 12555 Berlin — <sup>2</sup>FORTH, P.O. Box 1527, 71110 Heraklion, Greece

The electronic structure and photochemical behavior of the DNA bases is topic of dozens of theoretical and experimental studies every year. Despite these efforts, there is no consensus about the electronic properties of the pyrimidine bases. We performed time-resolved photoelectron and mass spectroscopy to assign the electronic states involved in the excited state relaxation of thymine and cytosine. Through a comparison with theoretical work, we hope to establish whether state-of-the-art calculations are capable to predict the correct excited state properties.

MO 23.4 Thu 15:30 MER 02

**Rovibronic states of 1,2,3,4-Tetrahydrocarbazole revealed by high resolution electronic spectroscopy** — ●OLIVIA OELTERMANN<sup>1</sup>, CHRISTIAN BRAND<sup>1</sup>, LEO MEERTS<sup>2</sup>, and MICHAEL SCHMITT<sup>1</sup> — <sup>1</sup>Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf — <sup>2</sup>Radboud University Nijmegen, Institute for Molecules and Materials, Nijmegen

The rotationally resolved LIF spectrum of the electronic origin of 1,2,3,4-Tetrahydrocarbazole was measured in order to determine structural parameters in the ground and electronically excited state. Comparison of our experimental results and *ab initio* calculations reveals, that the saturated six-membered ring in Tetrahydrocarbazole has twist conformation in both states. It could be shown, that the lowest excited singlet state of 1,2,3,4-Tetrahydrocarbazole has <sup>1</sup>L<sub>a</sub> character and not <sup>1</sup>L<sub>b</sub>, like nearly all other indole derivatives, except for 2,3-Dimethylindole. The upper limit for energy difference between <sup>1</sup>L<sub>a</sub> and <sup>1</sup>L<sub>b</sub> can be estimated to be 1000 cm<sup>-1</sup>, with the <sup>1</sup>L<sub>b</sub> being structurally and energetically close to the intersection of both states.

MO 23.5 Thu 15:45 MER 02

**Rotationally resolved electronic spectroscopy of 1,4-benzodioxan: the anomeric effect in ground and electronically excited state** — ●CHRISTIAN BRAND<sup>1</sup>, THI BAO CHAU VU<sup>1</sup>, LEO MEERTS<sup>2</sup>, and MICHAEL SCHMITT<sup>1</sup> — <sup>1</sup>Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf — <sup>2</sup>Radboud University, Institute for Molecules and Materials, Nijmegen

The electronic origin of 1,4-benzodioxan and three vibrational bands have been investigated using rotationally resolved electronic spectroscopy. By comparison to *ab initio* calculations all observed features could be assigned to the twist-conformer. Examination of the inertial defect show that the molecule is more planar in the electronic ground state than in the electronically excited singlet state. This effect can be traced back to a competition between the anomeric effect comprising the non-bonding p-type oxygen orbital and the antibonding axial CH-bond and the  $\pi$ - $\pi$  interaction between the oxygen lone pair and the  $\pi$ -orbitals of the benzene ring.