

MO 26: Electronic Spectroscopy II

Time: Thursday 14:00–15:45

Location: F 107

MO 26.1 Thu 14:00 F 107

Threshold photoelectron spectrum of the methylene amidogen radical H_2CN and its isomers — ●FABIAN HOLZMEIER¹, MELANIE LANG¹, INGO FISCHER¹, ANDRAS BODI², and PATRICK HEMBERGER² — ¹Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, 97074 Würzburg, Germany — ²Swiss Light Source, Paul-Scherrer-Institut, 5232 Villigen PSI, Switzerland

As bio-fuels become more and more important, the investigation of their combustion mechanisms is of great interest. Therefore, the characterization of possible nitrogen-containing combustion products is necessary. One of those nitrogen-containing intermediates is the methylene amidogen radical. This radical was generated by flash pyrolysis of methylhydrazine. In an iPEPICO-experiment (imaging Photoelectron Photoion Coincidence) at the Swiss Light Source synchrotron a mass-selected threshold photoelectron spectrum was obtained. The spectrum shows multiple different features, which can be assigned to four different isomers of the sum formula H_2CN : H_2CN , cis-HCNH, trans-HCNH, and H_2NC . In addition, the structure of a cationic transition state on the singlet potential energy surface was identified in the photoelectron spectrum. The experiment was validated by quantum chemical calculations and Franck-Condon-simulations. Hence, adiabatic ionization energies of the methylene amidogen radical and its isomers were determined.

MO 26.2 Thu 14:15 F 107

Photoionization and Photodissociation of Halogenated Sulfur Compounds — ●BEATE KIELING, LORYN FECHNER, FELIX GERKE, BURKHARD LANGER, ROMAN FLESCHE, and ECKART RÜHL — Physikalische Chemie, Freie Universität Berlin, Germany

Inner shell excitation of several sulfur(VI) and sulfur(IV) compounds containing halogens (SO_2F_2 , SF_4 , SOCl_2 , SOClF , SOF_2) is studied in the S 2p regime by using high-resolution synchrotron radiation and time-of-flight mass spectrometry. The photoabsorption, photoionization, and subsequent fragmentation of these species is investigated. The main objective of this work is a comparison of these compounds with sulfur hexafluoride (SF_6). The electronic properties of SF_6 are dominated by geometric cage effects leading to potential barriers with respect to photoionization. The interplay between outgoing and back-scattered electronic waves is reflected in the inner-shell spectra by (a) intense back-scattering *shape* resonances and (b) strongly suppressed Rydberg transitions. However, research regarding the inner-shell excitation of chemically related halogen-containing sulfur species is scarce. This is motivation for the present study on sulfur-halogen compounds that derive from SF_6 and SF_4 by substitution of fluorine atoms by oxygen and chlorine. Rydberg and shape resonances are observed which differ significantly from those in SF_6 . In addition, photoelectron-photoion-photoion coincidence (PEPIPICO) spectra are discussed, yielding a consistent picture of decay processes occurring in the S 2p regime.

MO 26.3 Thu 14:30 F 107

Unimolecular Reaction Mechanism of an Imidazolin-2-ylidene: An iPEPICO Study on the Complex Dissociation of an Arduengo-type Carbene — ●PATRICK HEMBERGER — Paul Scherrer Institut, Villigen, Switzerland

The photoionization and dissociative photoionization of 1,3-di-isopropylimidazolin-2-ylidene, was investigated by imaging photoelectron photoion coincidence (iPEPICO) with VUV synchrotron radiation. Only 0.5 eV above the adiabatic ionization energy the carbene fragments, yielding propene or a methyl radical in a parallel dissociation. Both reaction channels appear at almost the same photon energy, suggesting that they share the transition state. This is confirmed by calculations, which reveal the rate determining step as hydrogen migration from the iso-propyl group to the carbene center forming a resonance stabilized imidazolium ion. Above 10.5 eV, analogous sequential dissociation channels open up. The first propene-loss fragment ion dissociates further and another methyl or propene is abstracted. Again a resonance stabilized imidazolium ion acts as intermediate for this reaction. The aromaticity of the system is enhanced even in vertical ionization. Indeed, the coincidence technique confirms that a real imidazolium ion is produced by H-transfer over a small barrier. The

simple analysis of the breakdown diagram yields all the clues to disentangle the complex dissociative photoionization mechanism of this intermediate sized molecule. iPEPICO is a promising tool to unveil the fragmentation mechanism of larger molecules in mass spectrometry.

MO 26.4 Thu 14:45 F 107

Manipulation of electronically excited states of indole — ●CHRISTIAN BRAND, MARTIN WILKE, JOSEFIN ROLF, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The electronic origins of several singly substituted indole derivatives were investigated with rotationally resolved electronic spectroscopy. From the experimentally determined transition dipole moment orientation in combination with high level *ab initio* calculations the nature of the respective states was elaborated. It could be shown that a substituent at the biologically important position 5 at the indole chromophore has a pronounced influence on the photophysics of indole. Comparing the influence of substituents with different characteristics to each other yields that mesomeric effects have a greater impact on the energetic position of the excited states than inductive effects. Recently, these investigations were expanded to other positions at the chromophore. A thorough understanding of these influences may allow for a systematic manipulation of the electronically excited states.

MO 26.5 Thu 15:00 F 107

Rotationally resolved electronic spectroscopy of hydroxy-substituted indoles and determination of the characteristics of the electronically excited states. — ●MARTIN WILKE, OLIVIA OELTERMANN, CHRISTIAN BRAND, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The electronic origin of two bands of deuterated and undeuterated 5-hydroxyindole and a mixture of deuterated isotopomers of 6-hydroxyindole have been investigated using rotationally resolved electronic spectroscopy. By comparison of the experimental results to *ab initio* calculations the two undeuterated 5-hydroxyindole bands could be assigned to the syn- and anti-conformer. Furthermore, it could be shown that the lowest excited singlet state of the two rotamers has L_b character. A further approval for this assumption comes from the change of the angle between the inertial a-axis and the transition dipole moment vector due to deuteration. On the basis of the rotational constants the two deuterated bands could be identified as the O- and C3- deuterated molecules of 5-hydroxyindole. The calculations of 6-hydroxyindole show a mixed character of the first excited singlet state, so that an unambiguous assignment to L_b or L_a is not possible.

MO 26.6 Thu 15:15 F 107

Characterization of the electronically excited states of methoxy-substituted indoles by high resolution electronic spectroscopy — ●JOSEFIN ROLF, CHRISTIAN BRAND, OLIVIA OELTERMANN, MARTIN WILKE, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The rotationally resolved LIF spectra of several methoxyindoles were measured in order to determine the electronic nature of the lowest excited singlet states. Comparison of our experimental results to the *ab initio* calculations reveals a strong dependence of the transition dipole moment orientation on the respective structure for 4- and 6-methoxyindole. Moreover, the excitations to the S_1 and S_2 states are predicted to be heavily mixed. The difficult assignment of the electronic states to the L_a and L_b states based on the calculations are discussed.

MO 26.7 Thu 15:30 F 107

Dispersed fluorescence spectroscopy on 5-Cyanoindole — ●ANNE GRÄSSLE, BENJAMIN STUHLMANN, MICHAEL SCHMITT, and KARL KLEINERMANN — Heinrich Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

Indole is the chromophore of the aromatic amino acid tryptophan. The fluorescence of tryptophan is utilized in the spectroscopy of proteins.

The energetic order of the two first electronically excited singlet states of indole, L_a and L_b , strongly depends on the polarity of its environment, e.g. the hydrophile outer region or the hydrophobe inner

region of a protein: The L_a is stabilized by polar interactions because of its larger permanent dipole moment.

These electronic states can also be affected by the introduction of substituents with different inductive (and mesomere) effects in different positions. The cyano-group has a negative inductive effect and in the 5-position relative to the pyrrole-nitrogen it leads to a stabilization of

the L_a state.

We used high resolution dispersed fluorescence spectroscopy and laser induced fluorescence in order to determine the changes of the geometry upon electronic excitation using the rotational constants and the Franck-Condon factors of different $L_a \rightarrow S_0$ transitions of 5-cyano indole to confirm this hypothesis.