MO 2: Elektronische Spektroskopie

Zeit: Montag 16:30–19:00 Raum: 3F

MO 2.1 Mo 16:30 3F

State-dependent gerade/ungerade intensity ratios in the Auger spectrum of N_2 — •Ralph Püttner[1,2], Hironobu Fukuzawa[2], Xiao-Jing Liu[2], Sergey Semenov[3], Nikolai Cherepkov[3], Takahiro Tanaka[4], Masamitsu Hoshino[4], Hiroshi Tanaka[4], and Kiyoshi Ueda[2] — [1]Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany — [2]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan — [3]State University of Aerospace Instrumentation, 190000, St. Petersburg, Russia — [4]Department of Physics, Sophia University, Tokyo 102-8554, Japan

Auger spectra of the N $1s\sigma_{g,u}$ core holes in N_2 to five different quasi-stable final states are presented; they exhibit the gerade/ungerade splitting as well as vibrational progressions. The N $1s\sigma_g$/N $1s\sigma_u$ Auger intensity ratio depends on the final state. In particular, for the states $X\ ^1\Sigma_g^+$ and $D\ ^1\Sigma_u^+$ ratios of $\cong$2.1 and $\cong$0.8 are derived. These values are in agreement with *ab initio* calculations and the large value for the X state can qualitatively be related to the gerade or ungerade symmetry of the Auger electron. In addition, from the vibrational progressions in the Auger spectrum, the vibrational energies $\hbar\omega$, the anharmonicities $x\hbar\omega$ and the equilibrium distances R_e for the dicationic final states are derived in a fit analysis assuming Morse potentials.

MO 2.2 Mo 16:45 3F

Vibrationally resolved C $1s^{-1}$ Auger spectrum of CO_2 — •Vladimir Sekushin[1], Ralph Püttner[1,2], Günter Kaindl[1], Xiao-Jing Liu[2], Hironobu Fukuzawa[2], Kiyoshi Ueda[2], Takahiro Tanaka[3], Masamitsu Hoshino[3], and Hiroshi Tanaka[3] — [1]Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan — [3]Department of Physics, Sophia University, Tokyo 102-8554, Japan

The high-resolution Auger spectrum of CO_2 subsequent to C $1s^{-1}$ photoionization is reported along with the corresponding photoelectron spectrum. Auger transitions to seven quasi-stable final states are observed. They are assigned on the basis of theoretical results in combination with the assumption that the Auger spectrum is dominated by transitions to singlet states. From a Franck-Condon fit analysis of the vibrational progressions in the Auger spectrum, the vibrational energies $\hbar\omega$, the anharmonicities $x\hbar\omega$ and the equilibrium distances R_e for the dicationic final states are derived assuming Morse potentials. The relative intensities of the various C $1s^{-1}$ Auger transitions are also obtained.

MO 2.3 Mo 17:00 3F

Angle sensitive Doppler-spectroscopy of inversion symmetric molecules — •Rainer Hentges[1], Axel Reinköster[1], Markus Braune[1], Sanja Korica[1], Burkhard Langer[2], Oliver Kugeler[3], Uwe Hergenhahn[4], and Uwe Becker[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Freie Universität Berlin — [3]BESSY GmbH, Berlin — [4]MPI für Plasmaphysik, Garching

One of the most intriguing effects of quantum mechanics is the tunneling and over the barrier reflection effect. Electron tunneling is the basis of the separation of the parity eigenstates in all homonuclear diatomic or, more general, inversion symmetric molecules. However, electron tunneling on real time scale became only very recently subject of experimental investigations. These investigations were still limited to tunneling barriers induced by the probe pulse. Natural barriers, such as the barriers between the two identical atoms in homonuclear molecules, have so far never been studied. We present the first results of indirect time resolved studies on the electron tunneling effect in O_2 and SF_6. Excitation of these molecules into dissociative excited states gives rise to autoionization of the dissociating system [1]. The fingerprint of this process is the Doppler-shift of the autoionizing electrons in the molecular frame. We show that the Doppler-shifted autoionizing lines provide a tool to study the fraction of core-holes which have been tunneled to the other atomic site of the homonuclear molecule during the deexcitation process. This is an indirect measurement of electron tunneling in homonuclear molecules.

[1] Björneholm et al., Phys. Rev. Lett. 84, 2826 (2000)

MO 2.4 Mo 17:15 3F

Interference effects in the photoelectron emission of inversion symmetric molecules — •Sanja Korica[1], Axel Reinköster[1], Markus Braune[1], Rainer Hentges[1], Burkhard Langer[2], and Uwe Becker[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Freie Universität Berlin

Inversion symmetric molecules generate eigenstates of the parity operator. These gerade and ungerade called eigenstates reflect the phase coupling between the atomic sites of the molecule, being either positive or negative. Photoelecton emission from these molecules gives rise to oscillating partial cross sections with a phase shift of π from these symmetry eigenstates. The oscillation period depends on the bond lengths of the corresponding molecules. Cohen and Fano [1] were the first who mentioned and analysed this phenomenon of wave like behavior of photoelectron emission. Regarding the de Broglie wavelengths of the emitted photoelectron there could be less than one period up to more than ten periods of oscillation depending on the photon energy range available for experimental investigations. We show that the study of the Cohen-Fano oscillations from molecular hydrogen to the bucky ball molecule C_{60} covers two orders of magnitude in oscillation periods. This shows that the Cohen-Fano model of wavelike emission for two indistinguishable emitter sites is an universal model.

[1] H. D. Cohen and U. Fano, Phys. Rev. 150, 30 (1966)

MO 2.5 Mo 17:30 3F

Time-resolved photoelectron spectroscopy of DNA base clusters — •Thomas Schultz[1], Elena Samoylova[1], Yuliya Rulyk[1], Hans-Herman Ritze[1], Wolfgang Radloff[1], and Ingolf Volker Hertel[1,2] — [1]Max-Born Institut Berlin, Max-Born-Strasse 2A, 12489 Berlin — [2]Fachbereich Physik der Freien Universität Berlin, Arnimallee 14, 14195 Berlin

The photochemistry of large molecules can be due to inherent properties of the light-absorbing chromophores, but can also be can be dominated by intermolecular interactions. The latter play a very important role in biological systems, where well defined structure often determines molecular function. We investigate the photochemistry, and in particular the photostability, of DNA building blocks in vacuo and try to reproduce structural features in small molecular clusters. Reaction and relaxation pathways can be mapped in real time by time-resolved pump-probe ionization and coincident detection of electrons and ions.

MO 2.6 Mo 17:45 3F

Transfer processes in organic donor-acceptor dyads containing tetraphenylbenzidine and perylenebisimide studied by time-resolved spectroscopy — •Christiane Hofmann[1], Peter Bauer[2], Mukundan Thelakkat[2], and Jürgen Köhler[1] — [1]Department of Experimental Physics IV and BIMF, University of Bayreuth, D-95440 Bayreuth, Germany — [2]Applied Functional Polymers, University of Bayreuth, D-95440 Bayreuth, Germany

We investigated transfer processes in organic donor-acceptor dyads by time-resolved fluorescence spectroscopy. In the dyads, perylenebisimide (PBI) is covalently linked to a tetraphenylbenzidine (TPD) unit by a spacer. TPD acts as an energy transfer donor, PBI as an acceptor. Fluorescence lifetimes of both TPD and PBI have been determined for three different types of spacer and as a function of the solvent. We found that changing the spacer length had a significant influence on the TPD lifetime and on energy transfer efficiency. For all three TPD-PBI dyads the PBI lifetimes were considerably shorter than those measured for pure PBI and varied significantly upon changing the chemical composition of the spacer. We could also show that the PBI lifetimes depend noticeably on the solvent. Particularly, we found a correlation between the acceptor decay rate and the rotational diffusion time constant, which in turn is a function of the local viscosity of the solvent.

MO 2.7 Mo 18:00 3F

The structure of cyclic azaindole-water clusters from rotationally resolved electronic spectroscopy — •Michael Schmitt[1], Thi Bao Chau Vu[1], Yuriy Svartsov[1], W. Leo Meerts[2], and Ivo Kalkman[2] — [1]Heinich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — [2]Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen

Azaindole has two possible sites for hydrogen bonding, one potentially acting as proton donor, the other as proton acceptor. This behaviour, which is shared with chromophores like 2-pyridone and 7-hydroxyquinoline opens the possibility to form chains of water molecules bridging the two binding sites. Since azaindole may exist in two tautomeric forms, 1*H*-7-azaindole (1*H*-pyrrolo[2,3-b]pyridine) and 7*H*-7-azaindole (7*H*-pyrrolo[2,3-b]pyridine) these water chains may be capable of inducing a proton transfer which interconverts the two tautomeric forms. The barriers for this proton transfer depend strongly on the number of water molecules in the chain and on the electronic state. In the talk we present our latest results on the structure and tunneling motions in the water clusters of azaindole from a comparison of rotationally resolved electronic spectroscopy to ab initio calculations.

MO 2.8 Mo 18:15 3F

High resolution spectroscopy of neurotransmitter analogues: tryptamine and 5-methoxytryptamine — •Thi Bao Chau Vu, Marcel Böhm, and Michael Schmitt — Heinich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

The activity of biomolecules depends strongly on their structure. In case of different confomers of neurotransmitters line serotonine or melatonine the questions arises which is the most stable one in aqueous solution. We investigated the structure and conformational stabilization of microsolvated complexes of tryptamine and 5-methoxytryptamine, the builing blocks of the above neurotransmitters by rotationally resolved electronic spectroscopy. In the present talk the results of these experiments will be presented and compared to the results of ab initio calculations.

MO 2.9 Mo 18:30 3F

Rotationally resolved electronic spectroscopy of the benzoic acid dimer — •Michael Schmitt[1], Thi Bao Chau Vu[1], W. Leo Meerts[2], and Ivo Kalkman[2] — [1]Heinich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — [2]Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen

The assignment and simulation of rotationally resolved electronic spectra gets more and more complicated with increasing molecule size, due to strongly overlapping transitions. Many automated fitting techniques for extraction of the molecular parameters from the spectra have often the disadvantage of being trapped in local minima. The use of genetic algorithms for fitting of the parameters in combination with a cost function for the fit, that allows for determination of similarities between experiment and simulation solves most of the above problems. The genetic algorithms show their full power with increasing complexity of the spectra and number of parameters to be fit. In the present talk I will present the application of the method to the interpretation of the rovibronic spectra of the benzoic acid dimer. The molecular structure in both electronic states as well as the H-bond tunneling dynamics will be discussed and compared to other homodimers, like the formic acid dimer.

MO 2.10 Mo 18:45 3F

Detection of dark states of porphyrins — •Andreas-Neil Unterreiner[1], Oliver Schalk[1], Helge Brands[1], and Silviu Balaban[2] — [1]Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, 76128 Karlsruhe — [2]Forschungszentrum Karlsruhe, Institut für Nanotechnologie, 76021 Karlsruhe

Porphyrins are known to exhibit two absorbing bands, the B-band in the visible (500-650 nm) and the Soret-band in the UV (420 nm). In order to explain ultrafast dynamics after excitation to the Soret band, dark states in its vicinity have been postulated. Here, we present the first direct observation of these states in 5,10,15,20-tetra-*p*-tolyl-21*H*,23*H*-porphyrin (TTP-H_2) and 5,10,15,20-tetra-*p*-tolyl-porphyrinato zinc II (ZnTTP) by means of pump-probe and transient anisotropy experiments. After excitation to the Q-band, the molecules were probed by NIR-pulses in the range between 950 and 1350 nm in order to study states of gerade-symmetry. Examination of transient spectra and anisotropy revealed the energies of the two lowest so called dark states. The experimental results are compared with predictions from theoretical calculations.