

MO 12: High Resolution Spectroscopy and Precision Experiments

Time: Wednesday 10:30–12:30

Location: S HS 002 Biologie

MO 12.1 Wed 10:30 S HS 002 Biologie

Rotationally Resolved Electronic Stark Spectroscopy of 2,3-Benzofurane — •MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, HILDA LARTIAN, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The electronic origin of 2,3-benzofurane has been investigated using high resolution laser induced fluorescence spectroscopy (HRLIF) to analyze its electronic nature. The obtained molecular parameters from evolutionary algorithms were compared to the results of *ab initio* calculations. To investigate the permanent dipole moments in the ground and first excited state a homogeneous field was applied, which lifts the M degeneracy due to the Stark effect. Finally, the orientation of the transition dipole moment for the monomer is discussed and compared to that of indole in particular.

MO 12.2 Wed 10:45 S HS 002 Biologie

Rotationally Resolved Electronic Stark Spectroscopy of 4-cyanoindole — •MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, HILDA LARTIAN, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

High resolution electronic Stark spectroscopy is a valuable tool to determine the electronic nature of substituted indoles. Both, 3- and 5-cyanoindole were already investigated via high resolution spectroscopy and the electronic nature of their first excited states were identified as L_b -state for 3-cyanoindole and L_a -state for 5-cyanoindole, respectively. Now, 4-cyanoindole and its N-deuterated analogon were studied, evaluated via evolutionary algorithms and compared to the results of *ab initio* calculations. The rotational constants, permanent dipole moments in the ground and first excited state, the orientation of the transition dipole moment and the fluorescence lifetime were determined and used to identify the lowest excited singlet state as a L_a -state. Finally a view on the diverging fluorescence lifetimes of different cyanoindoles is given in this talk.

MO 12.3 Wed 11:00 S HS 002 Biologie

Predicting *para-ortho* conversion in ammonia — •GUANG YANG^{1,4}, VINICIUS SILVA DE OLIVEIRA^{2,4}, CHRISTOPH HEYL², ANDREY YACHMENEV^{1,3}, INGMAR HARTL², and JOCHEN KÜPPER^{1,3,4} — ¹Center for Free-Electron Laser Science, DESY, Notkestrasse 85, Hamburg — ²DESY, Notkestrasse 85, Hamburg — ³The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, Hamburg — ⁴Department of Physics, University of Hamburg, Luruper Chaussee 149, Hamburg

We present a combined theoretical and experimental study of the hyperfine-resolved spectrum of ammonia and its deuterated isotopologues. The calculations have been performed using the variational approach TROVE, a new spectroscopically determined potential energy surface, and *ab initio* quadrupole, spin-spin, and spin-rotation coupling surfaces. The computed spectroscopic line lists cover transitions between levels with rotational excitations up to $J = 20$ and vibrational band centers with up to 8000 cm^{-1} above the zero-point-energy level.

For the spectroscopic observation of the *para-ortho* interconversion we use mid-infrared frequency comb spectroscopy in both ammonia vapour and a cold molecular beam. Furthermore, its modulation by external electric field is discussed. Our theoretical model, i.e., the underlying potential energy surface will be refined using the experimentally observed transitions.

MO 12.4 Wed 11:15 S HS 002 Biologie

Triphenylmethane and all-*meta tert*-butyl triphenylmethane dimers: Observation of an unusual C-H...H-C distance in the gas phase via stimulated Raman spectroscopy — •DOMINIQUE MAUE¹, DOMINIC BERNHARD¹, PATRICK H. STREBERT¹, SÖREN RÖSEL², PETER R. SCHREINER², and MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiserslautern, Germany — ²Organic Chemistry, JLU Gießen, Germany

Recently a dimerization of triphenylmethane (TPM) and all-*meta tert*-butyl triphenylmethane (T^t BuPM) has been observed in crystals which leads in the case of T^t BuPM to an unusually short C-H...H-C contact. In order to find out if this is a pure intrinsic behavior of the molecules, we report here on molecular beam investigations on isolated dimers

by applying stimulated Raman spectroscopy with our new Raman setup. In combination with DFT calculations (including dispersion corrections) the formation of the head-to-head motif in T^t BuPM under isolated conditions has been proven by selectively probing the Raman-active central aliphatic C-D vibration within the dimer of the singly deuterated monomers. This arrangement is driven by London dispersion involving the *tert*-butyl groups which outbalances their steric repulsion. It is a first example of this binding motif investigated in an isolated dimer in the gas phase. In the unsubstituted TPM dimer no such dispersion interaction is possible, thus a tail-to-tail structure is identified as the most stable arrangement.

MO 12.5 Wed 11:30 S HS 002 Biologie

Nuclear-quadrupole coupling effects in laser alignment of asymmetric top molecules — •LINDA V. THESING^{1,2,3}, ANDREI DUCHKO^{1,3}, ANDREY YACHMENEV^{1,2}, ROSARIO GONZÁLEZ-FÉREZ⁴, and JOCHEN KÜPPER^{1,2,3,5} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Center for Ultrafast Imaging, Universität Hamburg, Germany — ³Department of Physics, Universität Hamburg, Germany — ⁴Instituto Carlos I and Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, Spain — ⁵Department of Chemistry, Universität Hamburg, Germany

We present a theoretical time-dependent study of the field-free alignment of asymmetric top molecules taking into account the hyperfine coupling due to nuclear-quadrupole interactions. It was recently shown that the nuclear-quadrupole coupling influences the impulsive alignment of linear I_2 molecules on an experimentally relevant timescale [1]. Here, we analyze the field-free alignment dynamics, induced by a truncated laser pulse, for the prototypical iodobenzene and diiodobenzene molecules, unraveling the effects of the nuclear-quadrupole coupling. These theoretical studies illustrate how the coupling strength, the number of strongly coupled nuclei and rotational constants affect the alignment revival structure obtained for the different molecules.

[1] Thomas et al., *Phys. Rev. Lett.* **120**, 163202 (2018)

MO 12.6 Wed 11:45 S HS 002 Biologie

Rotational spectroscopy of molecular ions with 3×10^{-12} resolution and 1×10^{-10} precision — SOROOSH ALIGHANBARI¹, GOURI GIRI¹, FLORIN CONSTANTIN^{1,2}, MICHAEL HANSEN¹, VLADIMIR KOROBOV³, and •STEPHAN SCHILLER¹ — ¹Heinrich-Heine-Universität Düsseldorf — ²PhLAM, Univ. Lille, Villeneuve d'Ascq — ³Joint Inst. for Nucl. Research, Dubna

Trapped and sympathetically laser cooled molecular ions can be spectroscopied with high spectral resolution. So far, however, the achieved linewidths were limited by the residual Doppler broadening present even at the mK - level temperatures reached in traps. In the case of rotational spectroscopy, with its large transition wavelengths, it is possible to take advantage of the confinement of the trapped ion ensemble in the directions transverse to the trap axis. It is then possible to reach the Lamb-Dicke regime, with a strong reduction in linewidth.

We demonstrate this on the molecular hydrogen ions HD^+ , whose fundamental rotational transition frequency is at 1.3 THz. We observe transition linewidths as small as 4 Hz. We fully resolve the hyperfine spectrum. We also measure the transition frequencies in absolute terms. We are then able to determine the precision of our technique by comparing the measured frequencies with the predictions from very accurate *ab initio* theory. We find agreement at the fractional level of 1×10^{-10} . This represents the most accurate comparison of a molecular physics prediction with experiment.

Finally, we measure some hyperfine energies with lower experimental uncertainty than the theoretical prediction.

MO 12.7 Wed 12:00 S HS 002 Biologie

Electronic Structure Theory for Molecular Precision Tests of New Physics — •KONSTANTIN GAUL and ROBERT BERGER — Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

Detection of simultaneous violation of parity (\mathcal{P}) and time-reversal (\mathcal{T}) symmetry can imply physics beyond the Standard Model of particle physics. Permanent electric dipole moments (EDMs) violate both \mathcal{P} - and \mathcal{T} -symmetry. EDMs of elementary particles or nuclei and \mathcal{P}, \mathcal{T} -odd electron-nucleus current interactions can induce a permanent

EDM in atoms and molecules. Due to enormous electronic structure enhancements of \mathcal{P} , \mathcal{T} -odd effects in polar molecules, low-energy high-precision experiments on these molecules can give access to the TeV energy-regime. These precision tests are the most promising experiments for a first measurement of a permanent EDM the electron[1].

We discuss requirements of molecules for those high-precision measurements that aim to find new physics. Trends of \mathcal{P} , \mathcal{T} -violation within the periodic system of elements determined with quasi-relativistic calculations[2] are discussed and measurement models for disentanglement of sources of \mathcal{P} , \mathcal{T} -violation in molecules are presented[3]. Simple analytical models, which are gauged by *ab initio* calculations, help to choose promising molecules for future experiments.

[1] ACME collaboration, Nature 562, 355 (2018).

[2] K. Gaul et. al., J. Chem. Phys. 147, 014109 (2017).

[3] K. Gaul et. al., arXiv:1805.05494, arXiv:1811.05749.

MO 12.8 Wed 12:15 S HS 002 Biologie

The observation of non-adiabatic alignment of gas-phase molecules via an adapted opto-galvanic technique. — CHRISTIAN MATTHAEI^{1,2}, MATTHEW S. ROBINSON¹, and MARKUS GÜHR¹

— ¹Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany — ²Current Address: Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Germany

We have developed a new method for observing the non-adiabatic alignment of gas-phase molecules via an adapted opto-galvanic technique, in which the critical components of the detector are an oscilloscope and a 9V battery. In this talk I will discuss how we were able to observe the rotational wavepacket revivals of N₂ and O₂ molecules in a near-atmospheric pressure air mixture, after excitation by an ultrafast laser pulse, with high precision using this technique.