

MO 7: High Resolution Spectroscopy

Time: Monday 16:15–17:45

Location: PA 1.150

MO 7.1 Mon 16:15 PA 1.150

Dipole Moments of Anisole in Ground and Excited State via Condensed Phase Thermochromic Spectroscopy and Gas Phase HRLIF Spectroscopy — ●MIRKO LINDIC, MICHAEL SCHNEIDER, MARIE-LUISE HEBESTREIT, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The dipole moment of anisole in ground and first excited singlet states was investigated and compared for the gas and the condensed phase. The dipole moments in solution have been determined using the method of thermochromic shifts of the fluorescence emission and absorption spectra. To test the validity of the method the simple model molecule anisole was measured with temperature dependent UV/Vis-absorption and fluorescence spectroscopy. Contrary to previous studies, the solvent cavity volume was determined experimentally via concentration dependent density measurements. To create exact values for comparison with those from the condensed phase high resolution laser induced fluorescence Stark spectra have been measured in order to reliably determine the excited state dipole moments for a direct comparison. A critical survey about the method will be given.

MO 7.2 Mon 16:30 PA 1.150

High-Resolution CARS Spectroscopy of the T₂ molecule — ●MAGNUS SCHLÖSSER¹, XIAODONG ZHAO¹, MADHU TRIVIKRAM², WIM UBACHS², and EDCEL J. SALUMBIDES² — ¹Tritium Laboratory Karlsruhe, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany — ²LaserLaB and Department of Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands

Molecular hydrogen is a benchmark system for bound state quantum calculation and tests of quantum electro-dynamical effects. While spectroscopic measurements on the stable species have progressively improved over the years, high-resolution studies on the radioactive isotopologues T₂, HT and DT have been limited. For this reason, we have built a high-resolution coherent anti-Stokes Raman spectroscopy system using nano-second pulses at the LaserLab Amsterdam and equipped it with a specially designed gas cell filled with < 1 GBq of T₂ from the Tritium Laboratory Karlsruhe. Here, we present an accurate determination of T₂ ($Q(J = 0 \dots 5)$) transition energies in the fundamental vibrational band of the ground electronic state, with the present experimental uncertainty of 0.02 cm⁻¹, which is a fivefold improvement over previous measurements, agreement with the latest theoretical calculations is demonstrated.

MO 7.3 Mon 16:45 PA 1.150

Precision Spectroscopy of the Hydroxyl Radical — ●ARTHUR FAST¹, JOHN E. FURNEAUX², and SAMUEL A. MEEK¹ — ¹Max Planck Institute for Biophysical Chemistry, Germany — ²University of Oklahoma, USA

We present results on optical frequency comb referenced spectroscopy of the $A^2\Sigma^+, v' = 0 \leftarrow X^2\Pi_{3/2}, v'' = 0, J'' = \frac{1}{2}$ transitions in OH. The comb spans from 1064 nm to 532 nm and is locked to a Nd:YAG laser. This laser is, in turn, stabilized to a molecular iodine transition using saturated absorption spectroscopy, resulting in a relative short-term stability of better than 10⁻¹². The A-X transitions near 308 nm are measured using laser-induced fluorescence in a supersonic molecular beam. The spectroscopy laser is a frequency-doubled CW dye laser which is directly stabilized to the comb. A sub 100 kHz measurement precision allows us to determine the spectroscopic constants much more precisely, up to two orders of magnitude better than the current literature values.

MO 7.4 Mon 17:00 PA 1.150

Observation of 1,2-, 1,3- and 1,4-dimethoxybenzenes via high resolution laser induced fluorescence Stark spectroscopy — ●MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, CHRISTIAN HENRICHS, and MICHAEL SCHMITT — Institute for Physical Chemistry I,

Heinrich-Heine-University, Düsseldorf

The different rotamers of 1,2-, 1,3- and 1,4-dimethoxybenzene were investigated using high resolution laser induced fluorescence spectroscopy. The molecular parameters, obtained from fit using a evolutionary strategies were compared to the results of *ab initio* calculations and used for structural assignment. To investigate the permanent dipole moments in the ground and first electronically excited singlet state, a homogeneous field was applied, which lifts the *M* degeneracy by the Stark effect. The resulting experimental permanent dipole moments were compared to predicted dipole moments via vectorial addition of the anisole dipoles and to the results of *ab initio* calculations.

Finally, the conformational space of 1,3-dimethoxybenzene is discussed in particular.

MO 7.5 Mon 17:15 PA 1.150

Probing a possible variation of the proton-to-electron mass ratio in the hyperfine-structure of ammonia, a theoretical study — ●ANDREI DUCHKO^{1,4}, ALEC OWENS^{1,2}, ANDREY YACHMENEV^{1,2}, and JOCHEN KÜPPER^{1,2,3,4} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Center for Ultrafast Imaging, Universität Hamburg, Germany — ³Department of Physics, Universität Hamburg, Germany — ⁴Department of Chemistry, Universität Hamburg, Germany

In this study we investigate a possible variation of the proton-to-electron mass ratio (μ) in the hyperfine transitions of the rovibrational spectrum of ammonia. The rovibrational spectrum has been computed variationally using the program suite TROVE [1,2], a new spectroscopically determined potential energy surface [3], and *ab initio* quadrupole [2], spin-spin, and spin-rotation coupling surfaces. The computed spectrum covers transitions between levels with rotational excitations up to $J = 15$ and vibrational band centers up to 8000 cm⁻¹ above the zero point energy. Comparison with experimental data confirms the high accuracy of the computed results, which is essential for modeling the hyperfine-resolved high-resolution spectra. We will present an extensive analysis of the μ -variation sensitivity coefficients of hyperfine transitions of ammonia in the microwave and infrared spectral regions.

[1] Yurchenko S. N., Thiel W., Jensen P., 2007, *J. Mol. Spectrosc.*, 245, 126. [2] Yachmenev A., Küpper J., 2017, *J. Chem. Phys.*, 147, 141101. [3] Coles, P., Yurchenko, S. N., Tennyson, J., 2017, in preparation

MO 7.6 Mon 17:30 PA 1.150

The role of dispersion in the structure of diphenyl ether aggregates — ●FABIAN DIETRICH¹, DOMINIC BERNHARD¹, MARIYAM FATIMA², ANJA POBLOTZKI³, MARTIN SUHM³, MELANIE SCHNELL², and MARKUS GERHARDS¹ — ¹Physical Chemistry and Research Center Optimas, TU Kaiserslautern, Germany — ²DESY Hamburg, Germany — ³Physical Chemistry, University Göttingen, Germany

Dispersion interactions can play an important role to understand unusual binding behaviors. This is illustrated here by a systematic study on the structural preferences of diphenyl ether (DPE)-alcohol aggregates, for which either an OH-O or an OH- π bound isomer can be formed. The alcohol molecules range from methanol to adamantanol. Investigations of the DPE-water complex complete this series. The experimental investigations are performed by IR/UV-methods, microwave spectroscopy, and FTIR spectroscopy, tightly connected with a detailed theoretical analysis. The resulting solvent-size-dependent trend on the structural preference turns out to be counter-intuitive, i.e., the hydrogen-bonded OH-O structures become more stable for larger alcohols, which are expected to be stronger dispersion energy donors and thus should prefer an OH- π arrangement. Quantification of dispersion interactions in combination with the twisting of the ether upon solvent aggregation are found to be a key for understanding this preference.