MO 51 Molecular Quantum Control

Zeit: Donnerstag 10:40–12:40 Raum: H12

MO 51.1 Do 10:40 H12

Population transfer in the multi-photon excitation of molecules — •Volker Engel, Marco Erdmann, and Stefanie Gräfe — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland,*D-97074 Würzburg, Germany

The laser induced selective preparation of electronically excited molecular states is investigated, where the instantaneous dynamical response of the system to an applied field is employed to determine the latter. By construction, the obtained pulses carry the signature of the electronic and nuclear motion [1]. It is shown that an effective population transfer to different target states is possible. Time-dependent photoelectron spectra are calculated to illustrate that the achieved control yields can be measured directly [2].

[1] S. Gräfe, C. Meier, and V. Engel, J. Chem. Phys. **122**, 184103 (2005).
[2] S. Gräfe, M. Erdmann, and V. Engel, Phys. Rev. A **72**, 013404 (2005).

MO 51.2 Do 10:55 H12

Pulse shaping control of spatially aligned rotational wavepackets of N_2 and O_2 — •Christian Horn[1], Marc Krug[1], Matthias Wollenhaupt[1], Thomas Baumert[1], Rebeca de Nalda[2], Florian Ausfelder[2], and Luis Banares[2] — [1]Universität Kassel, Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Heinrich-Plett-Str. 40, D-34132 Kassel, Germany — [2]Dpto. Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

Molecular alignment induced by ultrashort laser pulses has proven to be a powerful tool to create spatially aligned distributions in an otherwise randomly oriented, gaseous sample of molecules. The field-free alignment occurring at revivals of the rotational wave-packet is characterized by very fast dynamics where diatomic molecules oscillate between the situation of alignment (molecular axis preferentially oriented along the direction of the laser polarization vector) and anti-alignment, where the molecular axis preferentially lies in the plane perpendicular to the polarization vector. Previous theoretical and experimental work has been devoted to affect the magnitude and intensity of such revivals by using either pairs, or sequences of pulses. A much more general approach to control is the use of pulse-shaping techniques. We show that phase-only shaping of pulses can be successfully applied to the control of alignment revivals. Specifically we are able to enhance alignment at the expense of anti-alignment or vice versa at a given revival by applying a suitable phase mask to the aligning laser pulse. The results of the experiment are compared with numerical simulations.

MO 51.3 Do 11:10 H12

Phase locked Pulse Pairs Spectroscopy on Halogens in solid Ar — •Heide Ibrahim[1], Mizuho Fushitani[1], Markus Gühr[1,2], and Nikolaus Schwentner[1] — [1]Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin — [2]Stanford Synchrotron Radiation Laboratory, Menlo Park, California 94025-7015

We used an unbalanced Michelson Interferometer to obtain phase locked pulse pairs (PLPP) for spectroscopy on halogens in rare gas matrices. The chirp difference between the two arms was optimized to match the electronic B state anharmonicity of the molecule. The decaying modulation contrast in the PLPP spectrum indicates a loss of electronic coherence in the range around 1 ps for Cl_2 [1] and Br_2 in an Ar matrix. From vibrational wavepacket revivals and focussing we determine the vibrational coherence time of Br_2 and Cl_2 in solid Ar to be 3 ps [1,2]. Comparison with simulations of the PLPP spectrum, taking only into account the B state absorbance, indicates a further contribution in the PLPP spectra, most likely from the lower lying A state continuum. Changing the relative phase of the two pulses allows us to prepare vibrational wavepackets predominantly composed of Zero Phonon Lines (weakly interacting with the matrix) or of Phonon Side Band (strong interaction)and thereby coherently control the molecule-lattice interaction.

[1] M.Fushitani, M.Bargheer, M.Gühr and N.Schwentner, PCCP, 7, 3143 (2005)
[2] M.Gühr, H.Ibrahim and N.Schwentner, PCCP, 6, 5353 (2004)

MO 51.4 Do 11:25 H12

Enhancement of Population Transfer and Coherent Vibrations in Nile Blue (LD 690) with Phase Modulated Femtosecond Pulses — •Jürgen Hauer, Tiago Buckup, and Marcus Motzkus — Philipps-Universität, Physikalische Chemie, D-35032 Marburg, Germany

Coherent control of vibrational modes is essential for manipulating photochemisty on ground and excited states. We present an open loop control scheme for mode selective excitation and also for population transfer to the excited state of a dye molecule (Nile Blue). In a spatial light modulator, a sinusoidal modulation is applied in order to obtain pulse trains with well defined spacings between the sub-pulses. We show that these pulse trains allow for a more effective population transfer to the excited state than a Fourier limited pulse of equal energy. Independently thereof, the amplitude of the skeleton mode in Nile Blue at 600 cm-1 is also increased by a factor of up to 1.5, depending on the pump wavelength. In order to explain the nature of the observed enhancement effect, we compare the amplification factor of pulse trains compared to unshaped pulses at different excitation wavelengths. We also perform a chirp scan on the pump pulse, indicating that either ground or excited state wavepackets are observed, depending on the pump wavelength.

MO 51.5 Do 11:40 H12

Selective Spectral Filtering of Molecular Modes in Solution Phase Using Optimal Control in Four-Wave-Mixing Spectroscopy — •J. Konradi, A.V. Scaria, A.K. Singh, and A. Materny — International University Bremen, Germany

Due to their many degrees of freedom, femtosecond time-resolved four-wave mixing (FWM) techniques like CARS (coherent anti-Stokes Raman scattering) give access to different aspects of ultrafast dynamics. While the temporal resolution is high in fs spectroscopy, the resulting signals only have a poor spectral resolution. Coherent control techniques using tailored laser pulses allow for a manipulation of molecular multi-mode dynamics. Recently, we have demonstrated, that by shaping the pulses using a learning-loop optimal control scheme, in the FWM-spectrum vibrational modes can be selectively enhanced or suppressed [1]. Here, the ratio of the signal intensities for different lines in the nonlinear Raman spectrum served as feedback signal for an evolutionary algorithm. In our contribution we will present our latest results on frequency selective femtosecond spectroscopy. We have applied the optimal control technique in combination with electronically resonant as well as nonresonant four-wave mixing processes. We will demonstrate that in both cases the spectral resolution can be improved considerably by keeping the temporal resolution high. In order to gain information about the fundamental mechanism behind the spectrum control, an analysis of the experimental data has been performed, which will be discussed in detail.

[1] J. Konradi, A. K. Singh, A. Materny, *Phys. Chem. Chem. Phys.*, **7**, 3574, (2005)

MO 51.6 Do 11:55 H12

Enhancement of Raman Modes in the Ground State of all-trans-β-Carotene by Coherent Control — •J. Hauer[1,2], H. Skenderovic[2,3], K.-L. Kompa[2], and M. Motzkus[1,2] — [1]Philipps-Universität, 35032 Marburg — [2]Max-Planck-Institut für Quantenoptik, 85748 Garching — [3]Institute of Physics, 10000 Zagreb

The vibrational ground state modes of β-carotene in solution are investigated with DFWM (degenerate four wave mixing) under resonant and non-resonant conditions in an open loop coherent coherent control experiment with a spatial light modulator. Two of the three excitation pulses in the sequence are phase modulated by a sine function in order to obtain pulse trains with a well defined spacing between the sub pulses. Comparing the transients after resonant and the non-resonant excitation reveals that modes are not only filtered out but under resonant conditions also enhanced in their intensity compared to the Fourier-limited case. As we demonstrated in an earlier work, no such effect is observed with a non-resonant DFWM-sequence. For a better understanding of this amplification, we conduct a conventional Pump/Probe experiment in an oxazine dye (LD 690). This allows us to demonstrate that the observed effects are due to an enhanced population transfer between electronic states and an increased vibrational coherence.

MO 51.7 Do 12:10 H12

Coherent Control with Actively Shaped Supercontinuum from a Photonic Crystal Fiber — •B. von Vacano, W. Wohlleben, and M. Motzkus — Phys. Chem., Philipps-Universität, 35032 Marburg

Coherent control aims at selectively manipulating quantum states through the interaction with laser light. To do this, broadband excitation sources are highly attractive, as ultrashort pulses offer many possible interfering quantum paths. It would be very desirable to extend the applicability of standard 100 fs - Ti:Sa-oscillators towards broadband excitation. This can be achieved by nonlinear broadening of the laser spectrum in a microstructured fibre into supercontinuum and subsequent compression.

We successfully employed the combination of broadband pulses from a photonic crystal fibre (PCF) and pulse shaping for coherently controlled nonlinear spectroscopy [1]. The pulse shaper not only manages to compress the PCF supercontinuum to 18 fs pulses but also to additionally manipulate the phase for quantum control experiments. This approach is demonstrated by single-beam coherent anti-Stokes Raman (CARS) microspectroscopy [2,3] and is due to its simplicity well suited for general applications in coherently controlled spectroscopy and microscopy.

[1] B. von Vacano, W. Wohlleben, M. Motzkus. *Optics Letters*, in press.
[2] N. Dudovich, D. Oron, Y. Silberberg. *Journal of Chemical Physics* 118 (20), 9208 (2003).
[3] B. von Vacano, W. Wohlleben, M. Motzkus. *Journal of Raman Spectroscopy*, in press.

MO 51.8 Do 12:25 H12

Neurale Netzwerke in der Optimalen Kontrolle — •Reimer Selle, Gerhard Vogt, Tobias Brixner und Gustav Gerber — Physikalisches Institut, Universität Würzburg, Am Hubland, 97074Würzburg, Germany

Evolutionäre Algorithmen haben zusammen mit der Formung ultrakurzer Laserpulse zu beachtlichen Erfolgen bei der optimalen Kontrolle chemischer Reaktionen und anderer quantenmechanischer Prozesse geführt. Unglücklicherweise lassen sich aus den optimalen Pulsformen nur sehr bedingt Rückschlüsse auf die wirksamen Kontrollmechanismen ziehen.
Nun lässt sich jedoch ein solches Optimierungsexperiment auch als eine Abbildung der vom Pulsformer generierten elektrischen Felder auf die gemessenen Observablen betrachten. Neuronale Netzwerke haben sich durch ihre hohe Genauigkeit als Werkzeug zur Approximieung solcher Abbildungen bewährt. Nach dem Durchlaufen eines Lernprozesses, während dessen Beispieldaten dieser Abbildung gelernt werden, ist das Netzwerk fähig, über diese Daten hinaus zu verallgemeinern.
Sowohl im Falle der Erzeugung der zweiten Harmonischen (SHG), als auch bei der laserinduzierten Fluoreszenz eines Laserfarbstoffs (NK88) konnte gezeigt werden, dass sich Neuronale Netzwerke zur Modellierung dieser Prozesse eignen.
Falls sich Neuronale Netzwerke auch bei der Modellierung von Prozessen bewähren, die typisch quantenmechanische Interferenzphänomene beinhalten, so könnten sie eine interessante Möglichkeit zur realistischen Modellierung von Experimenten bieten. Diese Modellierung könnte z.B. auch einen Beitrag zum Auffinden relevanter Kontrollparameter leisten.