

Gas Phase Dynamics in Small Molecules and Clusters: From Analysis to Control

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Small metal clusters and organometallic molecules are ideal model systems for the investigation of optimum control scenarios, because they exhibit a large number of bound-bound and bound-free electronic transitions, allowing the study of their vibration dynamics and photoinduced fragmentation by means of time-resolved multi-photon ionization spectroscopy combined with mass spectroscopy.

This presentation is devoted to the real-time analysis and control of the nuclear dynamics of small molecules and clusters by using tailored femtosecond laser pulses. First the vibrational dynamics of the bound electronic states of the homonuclear trimer Na_3 are presented, then the branching control of the pre-dissociated electronic states of the heteronuclear trimer Na_2K are treated, and finally results about the fragmentation control of photoexcited $\text{CpMn}(\text{CO})_3$ are presented.

Control of the population of bound electronic states. With unchirped fs-laser pulses and - at moderate laser intensities - a pronounced wavepacket motion was observed exhibiting the eigenfrequencies of the electronically excited B-state of the sodium trimer. When, however, 400 fs downchirped pulses were employed, oscillations corresponding to the vibrational frequencies of the electronic ground state appeared. This observation can be explained by the stimulated Raman effect: The leading blue spectral edge of the downchirped pulse creates a non-stationary wavepacket in the B-state of Na_3 , which is then dumped down by the following red spectral tail of the same pulse into the vibrationally excited part of the ground state.

Feedback control of the population and ionization in dissociative systems. An active control of the experiment by means of feedback optimization was carried out by exciting differently branching ionization and fragmentation pathways of photoexcited Na_2K and $\text{CpMn}(\text{CO})_3$. By using a spatial light modulator setup and by employing an evolutionary algorithm for optimizing the phase and amplitude of the applied laser field, the yield of the resulting parent and fragment ions could significantly be controlled, and intrinsic properties of the photo-induced process emerged in the resulting pulse sequences. In the Na_2K system, for example, the obtained light intensity sequences of the optimized pulses correspond very well to the sequential cross sections of the irradiated transitions; their temporal structure reflects the vibrational eigenfrequencies of the corresponding parent molecule or fragment. In the case of the $\text{CpMn}(\text{CO})_3$, femtosecond high resolution experiments were used to determine the underlying dynamics.

Acknowledgment.

This work was performed in the research group of Prof. Ludger Wöste at the Institute for Experimental Physics of the Free University Berlin and supported by the Deutsche Forschungsgemeinschaft within the SFB 450 research project. The theoretical

calculations elucidating the detailed reaction mechanisms were performed by the group of Prof. V. Bonacic-Koutecky (Humboldt University Berlin) and Prof. J. Manz (Free University Berlin).

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