Unraveling the structure-function relationship in chemistry.

Specific chemical reactivities of spatially separated 3-aminophenol conformers with cold Ca^+ ions

Most molecules exhibit multiple structural isomers, which have the same chemical formula and connectivities, but differ in the exact positions of their atoms or the orientation of functional groups. These isomers can often interconvert thermally and are difficult to isolate. Consequently, a precise characterization of their role in chemical reactions has proven challenging. We have probed the reactivity of specific conformers – rotational structural isomers – by using an experimental technique based on their spatial separation in a molecular beam using electrostatic deflection. The separated conformers react with a target of trapped laser-cooled ions. In the reaction of Ca^+ with 3-aminophenol, we find a twofold larger rate constant for the *cis* compared to the *trans* conformer, although these conformers differ only in the relative orientation of the O–H bond. This result is explained by conformer specific differences in the long range ion-molecule interaction potentials. Our approach demonstrates the possibility of controlling reactivity through selection of conformational states.

Recent progress in the cooling, manipulation, and control of isolated molecules in the gas phase has paved the way for the study of chemical processes at high levels of sensitivity, selectivity, and detail. Methods for slowing and merging of supersonic molecular beams have enabled precise characterizations of the role of collision energy and of the molecular quantum state in scattering and reactive processes. Recent experiments with trapped, translationally cold molecules and ions have provided insights into the quantum dynamics of chemical reactions and the subtleties of intermolecular interactions. These experiments have thus far been restricted to reactions involving atoms or small molecules with simple geometric and quantum structures. The vast majority of molecules, however, possess a plethora of internal degrees of freedom that are challenging to probe independently. In particular, polyatomic molecules usually exhibit many rotational isomers. These conformers interconvert with low thermal barriers through rotations of covalent bonds. We have developed experimental methods to spatially separate the individual conformers in a molecular beam, consisting of an electric deflector [1], the quadrupole focuser [2], and the alternating gradient decelerator [3]. These are the neutral-molecule equivalents of the bender, the ion guide, and the LINAC for charged particles, respectively.

Here, we exploit the spatially separated conformers to study specific conformational effects in bimolecular reactions with stationary targets of ultra-cold trapped ions [4] to gain insight into fundamental reaction mechanisms in chemistry. We introduce a distinct approach for the study of conformational effects and conformation-dependent reactivities, i.e. rate constants, in bimolecular reactions. A cold beam of 3-aminophenol was created by co-expanding the molecular sample at 150 °C with high pressure helium or neon gas into the vacuum, resulting in cold molecular beams with internal temperatures of about 1 K. We spatially separated the *cis* and *trans* conformers of 3-aminophenol (C_6H_7NO) by using the inhomogeneous static electric field

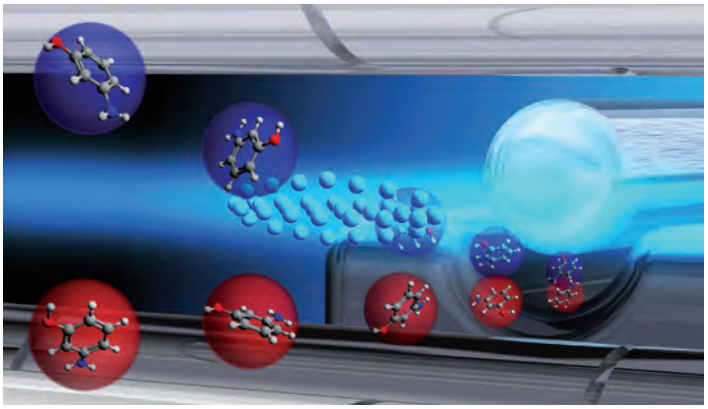

Figure 1

Artists impression of the experiment. A cold molecular beam of 3-aminophenol is dispersed in the electric deflector, samples of the separated *cis* and *trans* conformers are directed at a stationary Ca^+ ion target, and the rate of chemical reaction is recorded individually.

in the deflector and directed the molecules toward the reaction volume. There, they interacted with a stationary target of trapped and laser cooled Ca^+ ions. Reactions of organic molecules with metal ions are prototypical organometallic chemical processes that are relevant for the activation of chemically inert polar bonds, for instance, in catalysis, in atmospheric chemistry, and for the interaction of metal ions with biomolecular building blocks. The experiments were performed at CFEL and at the University of Basel.

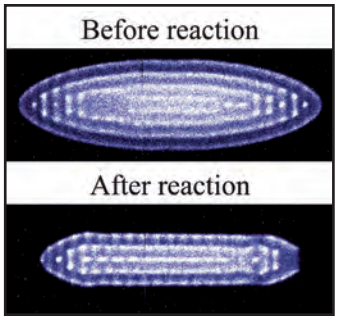

Figure 2

Atomically resolved fluorescence image of laser cooled Ca^+ ions in the trap. Heavier product ions collect at the outside of the Coulomb crystal; they are not resonant to the laser radiation and do not fluoresce.

Fig. 1 shows the experimental layout. The laser cooled Ca^+ ions, depicted by the small light-blue spheres, form a Coulomb crystal that provides a tightly confined reaction target, much smaller in extent than the conformationally separated regions of the dispersed molecular beam. The spatial separation of the conformers is depicted by the different trajectories of *cis* and *trans* 3-aminophenol by blue and red balls, respectively, which are overlayed by the actual molecular structures. The Coulomb crystal also provided a highly sensitive detection of reactions through the fluorescence of laser cooled Ca^+ ions, which was reduced for every single reaction, as the products are not resonant with the cooling lasers. Instead, they are sympathetically cooled to low translationally energies. In our experiments, the invisible products accumulated on the outside of the crystal and the Ca^+ ions formed a narrower cylinder in the centre of the crystal. These effects are shown in Fig. 2. The fluorescence depletion gave the reaction rate and the narrowing of the fluorescing volume shows that the reaction products are heavier than Ca^+.

In our benchmark experiment we applied various voltages to the electric deflector to vary the deflection and the dispersion of the two conformers. In Fig. 3 the data for experiments performed at one specific deflector voltage of 7.5 kV are shown as an example. In Fig. 3 (a) the individual molecular beam profiles for *cis* and *trans* 3-aminophenol are shown in blue and red, respectively, demonstrating the dispersion of the molecular beam. These curves were obtained by selective two-photon-ionization of the conformers using resonant ns laser pulses at 280 nm and vertically scanning the molecular beam across the laser focus. Subsequently, we measured the reactivity of the dispersed molecular beam with the stationary Ca^+ target, this time scanning the beam across the small trapped ion target. The resulting pseudo-first-order reaction rate constants are plotted in Fig. 3(b). The red and blue lines depict the fitted rate constant contributions from the *trans* and *cis* conformer, respectively. The considerably larger relative contribution from the *cis* species, compared to its ion signal in Fig. 3(a), already demonstrates its higher reactivity. A careful calibration of the molecular densities, pulse durations, and the electronic state populations of the Ca^+ ions allowed us to deduce the second order rate constants for the reaction.

The resulting second-order rates across the dispersed molecular beam are shown in Fig. 3(c). From this graph it is obvious that the *cis* conformer reacts about twice as fast as the *trans* conformer. The exact rate constants are $k_{2,cis} = (3.2 \pm 1.3) \times 10^{-9}$ cm^3 s^{-1} and $k_{2,trans} = (1.5 \pm 0.6) \times 10^{-9}$ cm^3 s^{-1} with a *cis:trans* reactivity ratio of 2.1 ± 0.5. A detailed analysis of the detuning of the cooling laser showed that more than 90 % of the reactions took place with electronically excited Ca^+; under these conditions the reaction was barrierless. We could explain the distinct reaction rates by capture rate calculations. These calculations predicted that the collision cross section is 1.5 times larger for *cis* than for *trans* 3-aminophenol due to differences in the respective charge-dipole interactions for the reaction systems.

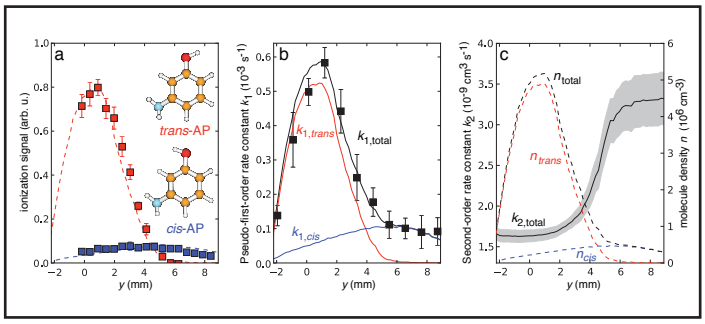

Figure 3

Experimental data: a) Conformer-specific molecular beam deflection profiles for a deflector voltage of 7.5 kV. This demonstrates the spatial dispersion of the conformers in the molecular beam. b) Reactivity as a function of the molecular beam composition. c) Second-order rate constants as derived from the calibrated experiment.

The present advances in the studies of chemical reactivities have become possible by combining conformer selection control experiments with highly sensitive trapped ion methods. We expect that the current methodology will benefit fundamental reaction-dynamics studies as well as the investigation of a wide range of ion-molecule reactions that are relevant for catalysis and interstellar chemistry. Electrostatic conformer selection is a widely applicable technique whenever the conformers present in the molecular beam possess sufficiently different dipole moments. Even more advanced electric field manipulation techniques for the separation of individual chemical species or individual quantum states have been demonstrated. In addition, sympathetic cooling of ions is a near-universal technique that allows the generation of Coulomb crystals of a wide range of atomic and molecular species with simultaneous preparation of their internal quantum state.

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