Communications

Pure Samples of Individual Conformers: The Separation of Stereoisomers of Complex Molecules Using Electric Fields

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Many complex molecules have multiple structural isomers; that is, multiple local minima on their potential energy surface. About twenty-five years ago, it was observed that multiple conformers of tryptophan are present even at the low temperatures of a few Kelvin in a supersonic jet.[1] These conformers have been studied extensively since then with sophisticated spectroscopic techniques. Individual conformers can be identified from their distinct electronic[1,2] or microwave[3] spectra. Information on the conformational structures can be obtained using microwave[4] or multiple-resonance infrared spectroscopy, for example.[5,6] In similar experiments it was even possible to obtain information on the barriers separating the conformers.[7]

The preparation of spatially separated conformers would provide unique possibilities for advanced further investigations. The chemical properties of the individual species and their differences could be directly studied in reactive scattering experiments. Such pure samples would also enable a new class of experiments, such as electron[8] and X-ray diffraction[9,10] or tomographic imaging[11] experiments of complex molecules in the gas phase. Molecular-frame photoelectron angular distributions, ultrafast time-resolved photoelectron spectroscopy, and ultrafast dynamics studies[12] would also benefit from the availability of these pure samples. For charged species, the separation of molecules with different shapes has been demonstrated by utilizing ion mobility in drift tubes.[13,14] For neutral molecules, the abundance of the conformers in molecular beams can be partly influenced by selective over-the-barrier excitation in the early stage of the expansion[15] or by changing the carrier gas.[16]

Herein, we demonstrate that electrostatic deflection, a classic molecular beam manipulation method that dates back to the 1920s,[17,18] allows the spatial separation of the con-

formers of a neutral molecule when it is applied to intense beams of rotationally cold molecules produced by a state-of-the-art pulsed supersonic expansion source.[19] The idea of exploiting electrostatic deflection to separate quantum states was already conceived by Stern in 1926 for light diatomic molecules,[20] and these ideas were recently extended to proposals for the separation of conformers of large molecules.[21,22]

Polar molecules experience a force in an inhomogeneous electric field. This force is due to the spatial variation in the potential energy of the molecules, and is given by $\vec{F} = \mu_{eff} \cdot \vec{\nabla} E$. The effective dipole moment μ_{eff} of a molecule in a given quantum state is the negative gradient of the potential energy with respect to the electric field strength E. This force has been used to decelerate small molecules in a supersonic jet to a standstill and subsequently trap them.[23] Similarly, large neutral molecules have been deflected,[22,24–26] focused,[27] and decelerated.[28] Passing polar molecules through a strong inhomogenous electric field will spatially disperse them according to their effective dipole moment. In particular, the conformers of a specific biomolecule all have the same mass m, but differ by the relative orientations of their functional groups. Typically, these functional groups have large local dipole moments associated with them, and the vectorial sum of these local dipole moments largely determines the overall dipole moment of the molecule.[29] Herein, we show that the resulting different overall dipole moments of the conformers can be exploited to select individual conformers using an electrostatic deflector.

The *cis* and *trans* conformers of 3-aminophenol (Figure 1) are used herein as prototypical structural isomers of complex molecules. From the precisely known rotational constants and dipole moments,[29] the energies of the rotational states of *cis*-3-aminophenol and *trans*-3-aminophenol are calculated as a function of electric field strength. Figure 1 shows the resulting Stark curves for the lowest rotational states of both species. From Figure 1, it is obvious that the effective dipole moments μ_{eff} of the states of *cis*-3-aminophenol are considerably larger than for *trans*-3-aminophenol, and therefore, a strong spatial separation of the conformers is expected. The results on the separation of the *cis* and *trans* conformers of 3-aminophenol are complementary to our previous experiments on the separation of the same species using an ac (alternating current) focusing device,[27] and we will briefly discuss the merits of the individual techniques in the Summary.

The experimental setup is shown in Figure 2, and a detailed description is given elsewhere.[22,26] 3-aminophenol (Sigma–Aldrich, 98%), seeded in 90 bar of helium, is released from a pulsed valve into high vacuum. The molecular beam is

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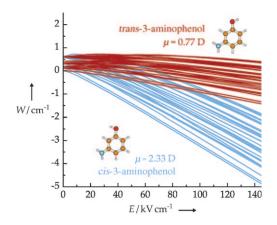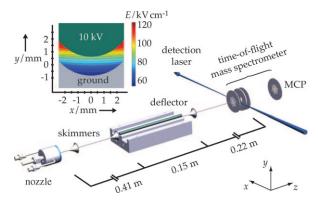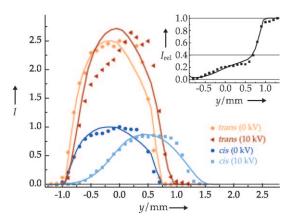Department of Physics and Astronomy, University of Aarhus

Figure 1. Molecular structures, dipole moments μ, and energies W of the lowest rotational states of *cis*- and *trans*-3-aminophenol as a function of the electric field strength E.

Figure 2. The experimental setup, consisting of the molecular beam source, the electrostatic deflector, and a photoionization time-of-flight mass spectrometer. Inset: a section through the deflector with a contour plot of the electric field strength.

Figure 3. Molecular beam intensity I as a function of the vertical position y of the detection laser for *cis*- and *trans*-3-aminophenol. Experimental data are given by symbols, and simulations by solid lines. The vertical profiles of the undeflected beams of *cis*- and *trans*-3-aminophenol are shown as circles (dark blue) and diamonds (orange), respectively. Squares (light blue) and triangles (red): corresponding deflection profiles with high voltage (10 kV) applied to the deflector. Inset: the fractional population I_{rel} of the *cis* conformer, which is obtained by dividing the *cis* intensity by the sum of the intensities of *cis* and *trans* at the respective height y; the horizontal line indicates the value in the original beam.

collimated using two skimmers before it enters the 15 cm-long electrostatic beam deflector. Inside the deflector an inhomogeneous electric field with a nearly constant gradient over a large area around the molecular beam axis is created. The deflector is mounted such that the deflection occurs vertically, and the 3-aminophenol molecules are deflected upwards. After passing the deflector, the molecular beam enters the target area, where it is crossed by a focused pulsed dye laser, which allows conformer-selective detection.
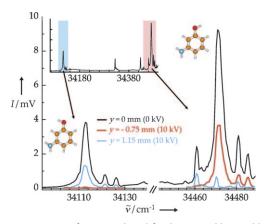
The spatial separation that is obtained is demonstrated by the conformer-selective deflection profiles in Figure 3. The density of a specific conformer[30] is measured as a function of the height y of the focused detection laser by a species-selective resonance-enhanced multiphoton ionization (REMPI) setup. When high voltages are applied to the deflector, both conformers are deflected upwards. However, the shift is considerably larger for the more polar *cis*-3-aminophenol, and above $y = 1$ mm a pure sample of *cis* conformers exists. Additionally, owing to the low internal temperature (ca. 1 K) of the initial molecular beam, the population of *cis*-3-aminophenol can be almost completely depleted for heights smaller than $y = -0.75$ mm, and an

almost pure sample of *trans*-3-aminophenol is obtained there. In the inset of Figure 3, the fractional intensity of the *cis* conformer in the deflected molecular beam is shown. It is clear that the fraction of *cis*-3-aminophenol in the probed sample can be continuously tuned by scanning the height of the probe laser focus, and importantly, at heights above the cut-off of the *trans*-3-aminophenol beam profile at $y = 1$ mm, the density of the *cis* conformers is still comparable to the density in the free jet.

The clean separation of the two conformers is also confirmed by the vibrationally resolved REMPI spectrum (Figure 4). The spectrum measured in the deflected part of the molecular beam ($y = 1.15$ mm) only contains bands arising from *cis*-3-aminophenol. In contrast, the spectrum measured in the depleted beam ($y = -0.75$ mm) shows only features that

Figure 4. UV spectra of 3-aminophenol for the original beam (black), the deflected ensemble (blue), and the depleted beam (red). The spectral signatures and the complete discrimination of the individual conformers are thus demonstrated.

can be assigned to the *trans* conformer. Of course, these conformer-specific UV spectra can also be obtained using double-resonance spectroscopy.[31] However, herein we obtain these spectroscopic signatures using a single laser to demonstrate the spatial separation of the conformers. Whereas the *trans*-3-aminophenol samples are still overlaid with seed gas from the molecular beam, the deflected *cis*-3-aminophenol sample is completely separated from *trans*-3-aminophenol molecules and the atomic seed gas. It should be pointed out that the lowest rotational states of *cis*-3-aminophenol, which are the most polar states, are deflected the most. These states can be aligned and oriented extremely well, providing the possibility for strong confinement of the rotational motion of the molecules.[22,26] It can be envisioned that this unprecedented control over the molecular ensemble can be exploited to perform stereospecific experiments on conformer- and state-selected samples.

In summary, we have demonstrated the spatial separation of individual conformers of 3-aminophenol using inhomogeneous electric fields using two different approaches, namely the deflection setup presented herein and the dynamic focusing setup demonstrated previously.[27] Both methods could be applied to many other molecules, including systems containing more than two conformers, as long as the temperature of the original beam is low enough.[22] However, there are profound differences between the two approaches: Whereas the ac focuser allows in principle all the conformers to be addressed individually, the deflector generally only separates off the most polar conformer. However, we have demonstrated herein that pure samples of other conformers can be created when appropriate experimental conditions are chosen. Moreover, in experiments with the focusing selector, the molecules are confined to the beam axis, resulting in a background of non-polar molecules and atomic seed gas. In contrast, the deflector separates the lowest rotational quantum states of the most polar conformer from any other species. Last but not least, it should be noted that the deflection experiment is technically considerably easier: the mechanical setup is much simpler and no high-voltage switching is required.

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