Spatially separated polar samples of the *cis* and *trans* conformers of 3-fluorophenol

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Abstract

We demonstrate the spatial separation of the *cis* - and *trans*-conformers of 3-fluorophenol in the gas phase based on their distinct electric dipole moments. For both conformers we create very polar samples of their lowest-energy rotational quantum states. A >95 % pure beam of *trans*-3-fluorophenol and a >90 % pure beam of the lowest-energy rotational states of the less polar *cis*-3-fluorophenol were obtained for helium and neon supersonic expansions, respectively. This is the first demonstration of the spatial separation of the lowest-energy rotational states of the least polar conformer, which is necessary for strong alignment and orientation of all individual conformers.

Keywords: 3-fluorophenol, cold molecules, Stark effect, molecular rotation, electric deflection, conformer separation

1. Introduction

Complex molecules often exhibit different structural isomers (conformers), even under the conditions of a cold molecular beam \[1\]. For a variety of upcoming novel experiments like photoelectron \[2,3\], electron \[4,5\], and x-ray diffraction \[6,7\] imaging of gas-phase molecules, for conformer-specific chemical reaction studies \[8\], or for mixed-field orientation experiments \[9,11\], pure species-selected molecular samples with all molecules in the lowest-energy rotational states are highly advantageous or simply necessary. Using strong inhomogeneous electric fields it is possible to spatially separate individual conformers \[12,13\], specific molecular clusters \[14\], as well as the individual quantum states of neutral polar molecules \[15,17\]. While the electric deflector was exploited for the spatial separation of individual conformers \[13\] and for the generation of highly polar samples of single-conformer molecules \[10\], it was not \textit{a priori} clear whether it would be possible to create pure samples of the most polar low-rotational-energy states of any conformer but the most polar one.

Here, we demonstrate the generation of conformer-selected and very polar ensembles of both conformers of 3-fluorophenol (C\textsubscript{6}H\textsubscript{5}OF, 3FP). 3FP is a prototypical large molecule with two stable conformers that differ by their orientation of the OH functional group. Conformer-selected and three-dimensionally oriented \[20\] ensembles of 3FP are good candidates for the investigation of conformer-interconversion reactions in an ultrafast laser pump, x-ray probe experiment, in which structural information would be accessible through photoelectron holography following F(1s) ionization \[2,6\].

The structures of \textit{cis} and \textit{trans} 3FP are shown in Fig. 1 together with calculated energies of their lowest rotational states in an electric field \[21\]. At relevant electric field strengths, all states are high-field seeking.

\textsuperscript{*}Molecules in high-field seeking states have a negative Stark energy shift, i.e., their potential energy decreases with electric field strength. Thus, they have positive effective dipole moments (\textit{vide infra}). Therefore, they orient along the electric field and they are attracted to regions of stronger electric field in order to minimize their energy.
moments of $\mu = 0.82$ D and 2.64 D for cis and trans, respectively, the energy dependence of the molecular eigenstates as a function of electric field strength is quite different for the two conformers. The projection of the molecule-fixed dipole moment onto the electric field axis is the effective dipole moment $\mu_{\text{eff}}$. The force exerted by an electric field on a polar molecule is $\vec{F} = -\mu_{\text{eff}}(\vec{e}) \cdot \nabla \epsilon$. Thus, for a given inhomogeneous electric field $\mu$-FP is deflected more than cis-3FP. Moreover, the lowest energy rotational states are generally more polar, i.e., have a larger effective dipole moment $\mu_{\text{eff}}$, than higher-energy rotational states [10] and, therefore, are deflected more.

2. Experimental details

Fig. 2 shows a schematic of the experimental setup [10]. In brief, 3FP was placed in a room-temperature Even-Lavie valve [22]. The molecules are coexpanded into the vacuum chamber at a repetition rate of 20 Hz in 50 bar of helium or 25 bar of neon, resulting in a supersonic expansion with a rotational temperature of the molecules of 1.5 K and 1 K, respectively. The molecular beam was collimated by two skimmers with diameters of 2 mm and 1 mm that were placed 5.5 cm and 21.5 cm downstream of the valve. Behind the second skimmer the molecular beam entered the electric deflector that provided an inhomogeneous electric field to disperse the molecular beam. A third skimmer with 1.5 mm diameter was placed directly behind the deflector. A time-of-flight mass-spectrometer was placed 30 cm downstream the deflector. A tunable pulsed dye laser (Fine Adjustment Pulsare Pro) provided approximately 400 $\mu$J per pulse in a soft focus at the electronic origin transitions of 36623 cm$^{-1}$ and 36830 cm$^{-1}$ for cis and trans, respectively [23]. Individual conformers were selectively detected through resonance-enhanced two-photon ionization (R2PI) mass spectrometry. For the measurements of spatial molecular beam profiles the laser is sampled by moving the focusing lens in steps of 200 $\mu$m in the y-direction.

Ab initio calculations (B3LYP/aug-cc-pVTZ) predict the trans conformer to be about 55 cm$^{-1}$ more stable than the cis conformer, in agreement with the 85 cm$^{-1}$ energy difference derived from a one-dimensionally torsional potential based on far-infrared spectroscopy [24]. The corresponding expected relative abundances of the trans and cis conformers in the molecular beam of approximately 2:1 agree with the experimentally obtained R2PI signal levels.

3. Results and discussions

Fig. 3 shows the vertical molecular beam profile for trans-3FP seeded in helium for different voltages applied to the deflector. The height of the undeflected molecular beam (0 kV) is 2 mm, defined by the mechanical apertures of the deflector and the skimmers. When a voltage of 5 kV is applied to the deflector the beam is deflected upwards by approximately 0.4 mm for the trans-conformer. Increasing the voltage to 10 kV and 14 kV, the deflection increases to 0.8 mm and 1.4 mm, respectively. Solid
lines show simulated spatial profiles obtained using the libcolmol package [16]. Only a single free parameter, the peak intensity of the undeflected beam, was adjusted to the experiment.

Fig. 4a shows the deflection profiles of both conformers of 3FP seeded in helium for applied voltages of 0 V and 14 kV to the deflector. The cis-conformer was deflected significantly less than the trans-conformer. This leads to a spatial separation of the trans-conformer from the cis-conformer and from the original beam, e.g., the seed gas. The purity of the trans sample at various heights is shown in Fig. 4b. Assuming similar excitation and ionization cross-sections for the two conformers, a beam of trans-3FP with a purity >95% was obtained in the range of 2.5 mm to 3.5 mm.

Around $y = -0.8$ mm a nearly pure beam of cis-3FP was obtained, similar to previous measurements [13]. However, these samples correspond to high-energy rotational states that are not suited for the envisioned novel orientation and imaging experiments. Moreover, these molecules were still immersed in the atomic seed gas. In order to create a pure beam of low-energy rotational states of cis-3FP we increased the deflection by seeding the molecules in neon, resulting in a molecular beam with a speed of 900 m/s, half the speed of the helium expansion. The doubled interaction time resulted in a stronger deflection, as shown in Fig. 5a. For an applied voltage of 14 kV both conformers were strongly deflected. For the originally very cold molecular beam the deflection of trans-3FP was so strong that most molecules crash into the rod electrode and are lost from the beam. For the cis conformer, however, a strong deflection out of the seed gas beam was observed. For $y = 1.5$–2.5 mm a beam of cis-3FP with a purity >90% with all molecules in the lowest-energy rotational states was obtained, see Fig. 5b, even though this conformer was less abundant in the original beam (vide supra). The remaining signal strength at position 1.5 mm was 40% of the maximum of the field-free case. The amplitudes for each conformer are normalized to the laser intensity. The remaining contribution from trans-3FP for $y < 2$ mm is attributed to warm molecules that diffuse into the detection region after colliding with the deflector rod.

4. Conclusions

In summary, we have demonstrated the spatial separation of the cis and trans conformers of 3FP and the generation of cold, low-energy rotational state samples of both conformers of 3FP. These results demonstrate the feasibility to create pure sam-
Figure 5: a) Field-free (0 kV) and deflected (14 kV) spatial beam profiles for the cis and the trans conformers of 3FP seeded in neon. b) The fractional population of the cis isomer in the beam.

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References

[1] T. R. Rizzo, Y. D. Park, L. Peteanu, D. H. Levy, Electronic spectrum of the amino acid tryptophan cooled in a supersonic molecular beam, J. Chem. Phys. 83 (1985) 4819–4820.

[2] F. Krasiqi, B. Najjari, L. Strüder, D. Rolles, A. Voitkiv, J. Ullrich, Imaging molecules from within: Ultrafast angström-scale structure determination of molecules via photoelectron holography using free-electron lasers, Phys. Rev. A 81 (2010) 033411.

[3] R. Boll, D. Anielski, C. Bostedt, J. D. Bozek, L. Christiansen, R. Coffee, S. De, P. Declève, S. W. Epp, B. Erk, L. Foucar, F. Krasiqi, J. Küpper, A. Rouzée, B. Rudenko, A. Rudenko, S. Schorb, H. Stapelfeldt, M. Stener, S. Stern, S. Techert, S. Trippeil, M. J. J. Vrakking, J. Ullrich, D. Rolles, Femtosecond photoelectron diffraction on laser-aligned molecules: Freeze frames of a molecular movie (2013). Submitted.

[4] G. Sciaini, R. J. D. Miller, Femtosecond electron diffraction: heralding the era of atomically resolved dynamics, Rep. Prog. Phys. 74 (2011) 096101.

[5] C. J. Hensley, J. Yang, M. Centurion, Imaging of isolated molecules with ultrafast electron pulses, Phys. Rev. Lett. 109 (2012) 133202.

[6] A. Barty, J. Küpper, H. N. Chapman, Molecular imaging using x-ray free-electron lasers, Annu. Rev. Phys. Chem. 64 (2013) 415–435.

[7] J. Küpper, S. Stern, L. Holmegaard, F. Filsinger, A. Rouzée, D. Rolles, A. Rudenko, P. Johnsson, A. V. Martin, M. Adolph, A. Aquila, S. Bajt, A. Barty, C. Bostedt, J. Bozek, C. Caleman, R. Coffee, N. Coppola, T. Delmas, E. S. Epp, B. Erk, L. Foucar, T. Gorkhover, L. Gumprech, A. Hartmann, R. Hartmann, G. Hauser, P. Holl, A. Hönke, N. Himmel, F. Krasiqi, K.-U. Kühl, J. Maurer, M. Messerschmidt, R. Moshammer, C. Reich, B. Ruden, R. Santra, I. Schlichting, C. Schmidt, S. Schorb, J. Schulz, H. Soltan, J. C. H. Spence, D. Starodub, L. Strüder, J. Thagsersen, M. J. J. Vrakking, G. Weidenspointner, T. A. White, C. Wunderer, G. Meijer, J. Ullrich, H. Stapelfeldt, H. N. Chapman, Coherent diffractive imaging of controlled ensembles of isolated gas-phase molecules (2013). Submitted, arXiv:1307.4577 [physics].

[8] Y.-P. Chang, K. Długołęcki, J. Küpper, D. Rösch, D. Wild, S. Willitsch, Specific Chemical Reactivities of Spatially Separated 3-Aminophenol Conformers with Cold Ca Ions, Science 342 (2013) 98–101.

[9] H. Stapelfeldt, T. Seidemann, Colloquium: Aligning molecules with strong laser pulses, Rev. Mod. Phys. 75 (2003) 543–557.

[10] L. Holmegaard, J. H. Nielsen, I. Nevo, H. Stapelfeldt, F. Filsinger, J. Küpper, G. Meijer, Laser-induced alignment and orientation of quantum-state-selected large molecules, Phys. Rev. Lett. 102 (2009) 023001.

[11] O. Ghafur, A. Rouzée, A. Gijsbertsen, W. K. Siu, S. Stölte, M. J. J. Vrakking, Impulsive orientation and alignment of quantum-state-selected NO molecules, Nat. Phys. 5 (2009) 289–293.

[12] F. Filsinger, U. Erlekam, G. von Helden, J. Küpper, G. Meijer, Selector for structural isomers of neutral molecules, Phys. Rev. Lett. 100 (2008) 133003.

[13] F. Filsinger, J. Küpper, G. Meijer, J. L. Hansen, J. Maurer, J. H. Nielsen, L. Holmegaard, H. Stapelfeldt, Pure samples of individual conformers: the separation of
stereo-isomers of complex molecules using electric fields, Angew. Chem. Int. Ed. 48 (2009) 6900–6902.

[14] S. Trippel, Y.-P. Chang, S. Stern, T. Mullins, L. Holmegaaard, J. Küpper, Spatial separation of state- and size-selected neutral clusters, Phys. Rev. A 86 (2012) 033202.

[15] J. Reuss, State Selection by Nonoptical Methods, in: G. Scoles (Ed.), Atomic and molecular beam methods, volume 1, Oxford University Press, New York, NY, USA, 1988, pp. 276–292.

[16] F. Filsinger, J. Küpper, G. Meijer, L. Holmegaard, J. H. Nielsen, I. Nevo, J. L. Hansen, H. Stapelfeldt, Quantum-state selection, alignment, and orientation of large molecules using static electric and laser fields, J. Chem. Phys. 131 (2009) 064309.

[17] S. Putzke, F. Filsinger, H. Haak, J. Küpper, G. Meijer, Rotational-state-specific guiding of large molecules, Phys. Chem. Chem. Phys. 13 (2011) 18962.

[18] A. I. Jaman, R. N. Nandi, D. K. Ghosh, Microwave spectrum of 3-fluorophenol, J. Mol. Spec. 86 (1981) 269–274.

[19] A. Dutta, A. I. Jaman, Microwave spectrum of cis 3-fluorophenol, Pramana – J. Phys. 24 (1985) 499–502.

[20] I. Nevo, L. Holmegaard, J. H. Nielsen, J. L. Hansen, H. Stapelfeldt, F. Filsinger, G. Meijer, J. Küpper, Laser-induced 3D alignment and orientation of quantum state-selected molecules, Phys. Chem. Chem. Phys. 11 (2009) 9912–9918.

[21] Y.-P. Chang, F. Filsinger, B. G. Sartakov, J. Küpper, CM1stark: Python package for the stark-effect calculation and symmetry classification of linear, symmetric and asymmetric top wavefunctions in dc electric fields, Comp. Phys. Comm. (2013). DOI: 10.1016/j.cpc.2013.09.001.

[22] U. Even, J. Jortner, D. Noy, N. Lavie, N. Cossart-Magos, Cooling of large molecules below 1 K and He clusters formation, J. Chem. Phys. 112 (2000) 8068–8071.

[23] E. Fujimaki, A. Fujii, T. Ebata, N. Mikami, Autoionization-detected infrared spectroscopy of intramolecular hydrogen bonds in aromatic cations. I. principle and application to fluorophenol and methoxypyphenol, J. Chem. Phys. 110 (1999) 4238–4247.

[24] A. S. Manocha, G. L. Carlson, W. G. Fateley, Barriers to internal rotation in some m-substituted phenols, J. Phys. Chem. 77 (1973) 2094–2098.

[25] L. Holmegaard, J. L. Hansen, L. Kalhøj, S. L. Kragh, H. Stapelfeldt, F. Filsinger, J. Küpper, G. Meijer, D. Dimitrovski, M. Abu-samha, C. P. J. Martiny, L. B. Madsen, Photoelectron angular distributions from strong-field ionization of oriented molecules, Nat. Phys. 6 (2010) 428.

[26] F. Filsinger, G. Meijer, H. Stapelfeldt, H. Chapman, J. Küpper, State- and conformation-selected beams of aligned and oriented molecules for ultrafast diffraction studies, Phys. Chem. Chem. Phys. 13 (2011) 2076–2087.