Studying rotational-state and conformational effects in chemi-ionisation reactions

A. Mishra[1], L. Ploenes[1], P. Stranak[1], C. He[1], S. K. Kim[2], S. Willitsch[1]*

[1]University of Basel, Department of Chemistry, Klingelbergstrasse 80, 4056 Basel, Switzerland, [2] KAIST, Department of Chemistry, Daejeon 34141, Republic of Korea

Conformers are the dominant isomers of complex molecules. The conformation of a molecule can have pronounced effects on its chemical reactivity. However, because they often interconvert into one another under ambient conditions, individual molecular conformations are difficult to isolate. Consequently, only sparse experimental data exists on the chemical properties of distinct conformers [1]. Over the past years, we have developed experimental methods to study conformational effects in ion-molecule reactions under single-collision conditions [2,3]. We have recently built a new crossed-molecular-beam setup to extend our methodology to neutral-neutral reactions [4]. This setup is equipped with an electrostatic deflector which enables the spatial separation of different conformers or individual rotational states of molecules based on their effective dipole moments. As the first application of this new method, rotational-state-dependent chemi-ionisation reactions of carbonyl sulfide (OCS) with metastable neon atoms were investigated. A pronounced state-specific effect on the product branching ratio was observed. Our result suggests that OCS molecules in the rotational ground state ? = 0 are a factor of 2.5 more reactive for dissociative ionisation than Penning ionisation compared to the ? = 1 state [4,5]. Moreover, for heavier molecules, the disentanglement of conformational and rotational-state effects can be difficult to analyse due to the involvement of several rotational states [5]. Choosing conformers that can be chemically separated and have high interconversion barriers could disentangle the conformational and rotational state dependencies. Therefore, we chose to study the chemi-ionisation reaction of 1,2-dibromoethylene (DBE), the conformers of which can be chemically separated [6,7]. Additionally, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are also currently undertaking a comparative study of the photochemistry, photoionization, and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene (DBE) as a prototypical system [8]. These investigations aim to gain a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity.

[1] S. Willitsch, *Adv. Chem. Phys.*, **2017,** 162, 307
[2] Y.-P. Chang, K. Dlugolecki, J. Küpper, D. Rösch, D. Wild, S. Willitsch, *Science*, **2013**, 342, 98
[3] A. Kilaj, J. Wang, P. Straňák, M. Schwilk, U. Rivero, L. Xu, O. A v. Lilienfeld, J. Küpper, S. Willitsch, *Nat. Commun*., **2021**, 12, 6047
[4] L. Ploenes, P. Straňák, H. Gao, J. Küpper and S. Willitsch, *Mol. Phys.*, **2021**, 119, 1965234
[5] L. Ploenes, P. Straňák, S. Willitsch, *in prep.*, **2022**
[6] W. Shi, R. H. Lipson, *Mol. Phys.*, **2007**, 105, 1701–1709
[7] T. Yamamoto, D. Kaneno, S. Tomoda, *Chem. Lett.*, **2005**, 34, 8
[8] J. Kim, S. -K. Kim, *J. Chem. Phys.*, **2021**, 155, 164304