## Background info (only in English)

<u>Non-ergodicity</u> Because ergodicity is a non-trivial mathematical concept, let us give a simple example from daily life for non-ergodic behavior in the way it is understood in chemistry. When you prepare a steak, you add salt and pepper to one side, fry it from one side for a short time (e.g. a minute), while adding spices to the other. Then you turn the steak, fry the other side for another minute and have a meal. If the steak were ergodic, the way of heating would matter and hence you could also fry it from one side only for 2 minutes. The result will be frustrating, however: burned from the bottom and still raw on the top. The physics behind it is that the heat transfer from the oil to the bottom side of the steak is faster than that within the meat.

In chemistry, the energy transfer within a molecule is usually much faster than that from or to the environment. Our examples with ion pairs thus mimic the situation of the frying steak in that the intramolecular energy transfer is hindered.

<u>Helquats</u> This new class of molecules has been discovered by Filip Teplý (IOCB, Prague). The helquats consist out of annelated rings which would overlap with each other in a planar arrangement and therefore they twist to a screw-like structure; like with real screws, the helquats exists as right- and left-handed enantiomers (so called "chiral" molecules). The name helquat goes back to the helical backbone on the one hand and the famous crop chemical paraquat.



<u>lon pairs</u> Normal molecules, for example water (H<sub>2</sub>O), have covalent bonds which can be imagined like a flexible stick connecting the atoms (i.e. H–O–H). In the case of ions, there exists another type of bonding which only results from the electrical charges. A naked sodium cation Na<sup>+</sup> and a chloride ion Cl<sup>-</sup> from regular rock salt, for example, form an ion pair of the type Na<sup>+</sup>···Cl<sup>-</sup>. In the ion pairs described above the interaction is diffuse and one can almost imagine it like the movement of two planets around each other.

<u>IR-Laser CLIO</u> The crucial experiments in the VIP paper forming the basis of the press release require an extremely strong laser in the range of infrared light. Currently, there exist only four such facilities worldwide, three of the in Europe. The intense laser irradiation allows to rapidly excite ("heat") mass-selected ions in an almost ideal environment without interactions to the outside. The infrared light of **m**ultiple **p**hotons then leads to ion **d**issociation, therefore the acronym of the technique is IRMPD. More: http://clio.lcp.u-psud.fr/clio eng/clio eng.htm

<u>ERC funding</u> The European Research Council aims to support frontier research in European science by specific funding of individual researchers without any quota for certain nations, regions or so. To this end, ERC grants with a volume of currently up to 3.5 M $\in$  per grant are given to European researchers. The grants run five years, thereby forming a firm basis to establish new concepts and ideas in scientific research. The evaluation of the applications at the ERC is extremely competitive and only based upon scientific criteria. More: http://erc.europa.eu/

<u>People involved</u> (in the order of the authorship)

*Christopher Shaffer* (US citizen) studied chemistry at the University of Wisconsin and presently is a postdoc at IOCB. He participated in the experiments at CLIO, performed most of the calculations, and was substantially involved in manuscript preparation.

*Ágnes Révész* (Hungarian) studied chemistry at the Eötvös Loránd University in Budapest, then made a postdoc at IOCB and presently has a position at the Hungarian Academy of Sciences. She participated in several missions to CLIO and established the mass spectrometry of helquats at IOCB.

*Detlef Schröder* (German) is a Distinguished Chair of IOCB. He studied chemistry in Berlin and took an independent position in Prague in 2006. Dr. Schröder holds the ERC Advanced Grant HORIZOMS. He led some of the missions to CLIO, directed this specific research, and wrote the article.

*Lukáš Severa* (Czech) studied chemistry at the Institute of Chemical Technology (Prague) and currently is a doctoral student at IOCB on the topic of organic synthesis with particular attention to helquats. He took care of the preparative aspects and performed some of the calculations.

*Filip Teplý* (Czech) is a team leader for organic synthesis at IOCB, who discovered the chiral helquat dications and as the discoverer had the privilege to name them. He guided the preparative aspects and participated in manuscript preparation.

*Emilie-Laure Zins* (French) studied chemistry at the Université Pierre et Marie Curie (Paris), afterwards made a postdoc at IOCB and then took a permanent position for infrared spectroscopy in Paris. She participated in several missions to CLIO.

*Lucie Jašíková* (Czech) studied chemistry at the Charles University (Prague) and then started her doctoral studies at the same university; presently, she is in maternity leave. She participated in several missions to CLIO, where she undertook isotopic studies.

*Jana* Roithová (Czech) has a research team at Charles University and currently leads the Department of Organic Chemistry. Doc. Roithová holds the ERC Starting Grant ISORI. She led some of the missions to CLIO and crucially contributed to the interpretation and manuscript preparation.