

## ♦ Magnetism in gold nanoparticles

Gold nanoparticles elicit an intense and very broad research activity because of their peculiar properties. Be it in catalysis, optics, electronics, sensing or theranostics, new applications are found daily for these materials. Approximately a decade ago a report was published with magnetometry data showing that gold nanoparticles, most surprisingly, could also be magnetic, with features that the usual rules of magnetism were unable to explain. Many ensuing experimental papers confirmed this observation, although the reported magnetic behaviours showed a great variability, for unclear reasons. Various theories have been put forth for explaining this unexpected magnetism but in spite of much effort, a totally satisfying explanation was still lacking as to why nanosized gold clusters could boast ferromagnetism above

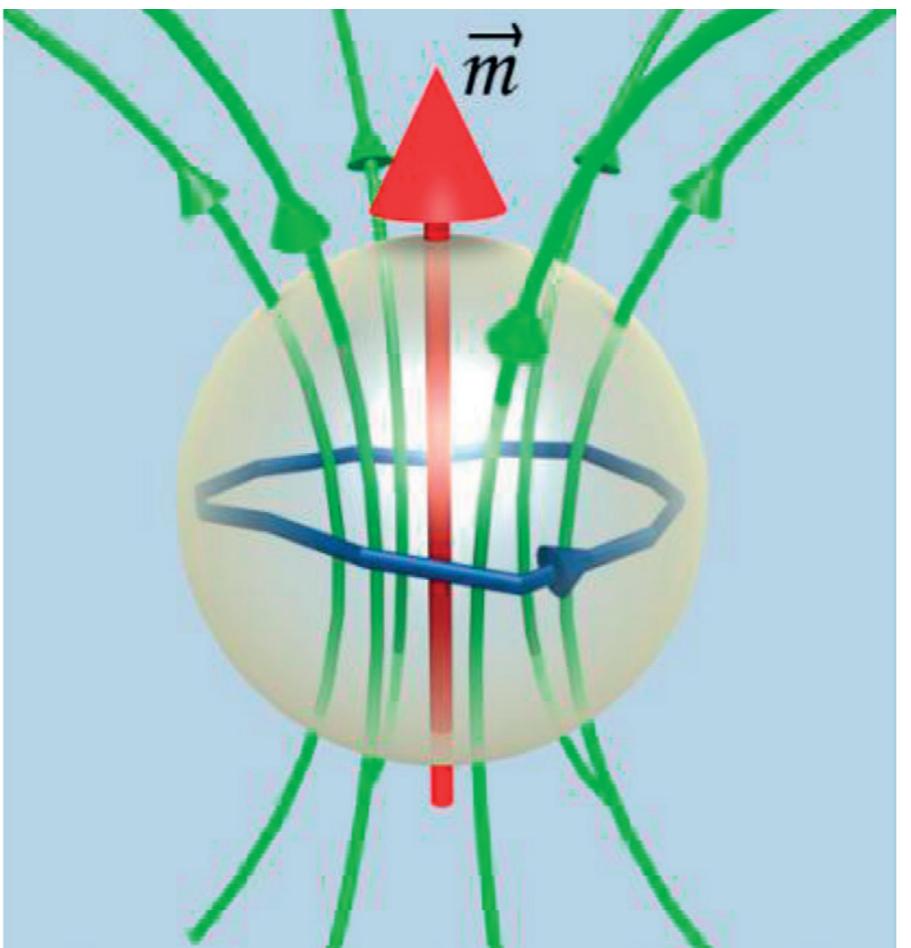
room temperature. The question is actually still hotly debated, mostly because there is a lack of global coherence: even though this unconventional magnetism has been proven beyond doubt, experiments exhibit a very poor reproducibility.

We have demonstrated that the observed magnetism could result from persistent currents and could therefore be of orbital nature, throughout the whole temperature range. Some very limited portions of a given sample, where the required conditions all are fulfilled locally, would even support *self-sustained* persistent currents, hence exhibit remnant magnetization and hysteresis. Our hypothesis would explain the magnetism, the lack of temperature dependence of the magnetic properties and why it has been impossible to detect a large enough

magnetic polarization on Au atoms with element-sensitive techniques such as XMCD (x-ray magnetic circular dichroism) or NMR (nuclear magnetic resonance). Moreover, the high variability of the observations would then be intrinsic, since it would stem from the statistical nature of the phenomenon, the magnetic response of a nanoparticle being, among others, function of the number of conduction electrons, which is clearly beyond control. Observing such a quantum effect at room temperature with user-friendly samples opens unforeseen new perspectives and new routes for the bottom-up fabrication of innovative magnetic materials made from non-magnetic elements. ■

G. L. Nealon, B. Donnio, R. Greget, J.-P. Kappler, E. Terazzi, and J.-L. Gallani, *Nanoscale*, 2012, **4**, 5244–58.

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◀ Schematic view of a nanoparticle developing a magnetic moment in response to a static external magnetic field.

# IPCMS News

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## Editorial

The contributions to the international newsletter of IPCMS presented in this issue exemplify the interdisciplinary and cross-fertilizing character of researches conducted at IPCMS in the fields of material science and nanoscience. In this framework, IPCMS activities are boosted by recent endeavors in biochemistry and biophysics, in the search of new design and functionalities at the molecular scale. Discoveries of new quantum phenomena are also to be emphasized.

As a revealing example at the interface between medicine and inorganic chemistry, the team of S. Bellemin has been able to improve the performances of metal-based pharmaceuticals via the introduction of suitable ligands, leading to two patents extended worldwide. In the contribution by J. Léonard and coworkers, the details of the molecular motion and vibrational wavepackets observed in biomimetic switches designed for conversion of light to mechanical energy are revealed.

The present issue of the IPCMS newsletter contains a breakthrough in the area of nanoscale magnetism, since the origin of magnetism in gold nanoparticles have been rationalized. The discovery of self-sustained persistent currents is found to be consistent with remnant magnetization and hysteresis, thereby explaining the lack of temperature dependence in the magnetization properties. An important electronic effect concerning the repartition of electronic waves in nanorings has been elucidated, i.e. "the whispering gallery effect" (contribution by the team of G. Schull). To this purpose, the team has synthesized nanorings of  $\pi$ -conjugated polymers on a gold surface. Researchers of IPCMS have also attained a breakthrough in the area of molecular electronics, by managing to obtain a deposited molecule prone to be used to encode information, since capable of adopting in a stable manner one high-spin state and one low-spin state (contribution by the team of M. Bowen).

Finally, an exciting new line of theoretical studies found recently its place at IPCMS with the arrival of Prof. Guido Pupillo and his team. Quantum many-body physical phenomena pertaining to the physics of cold atomic gases are being studied by focusing on low temperature systems with dominant dipolar interactions. The goal is to realize novel quantum phases and quantum simulations and computing.

The LabEX 'Nanostructures in Interaction with their Environment', headed by Jean-Yves Bigot (IPCMS) encompasses twenty-five PIs, and overall 40 members, the scientific perimeter being defined within the ISIS, ICS and IPCMS institutes.

Its aim is promoting cutting-edge, collaborative research on hot topics in nano science such as:

- Connecting nano-objects to the real world, from nano-objects to Nanotechnology
- Studying the fundamental interaction mechanisms, using photonic, magnetic, electronic, acoustic, mechanical probes with ultimate temporal and spatial resolutions
- Investigating the origin for the loss of information at the nanoscale (phase and energy relaxation, transfer of angular momentum)
- Using the "environment" to modify nano-materials (tuning material properties with external perturbations).

On June 19th, the Scientific Committee of the "laboratory of excellence" LabEX NIE met at IPCMS and awarded funding to seven projects selected among 25 proposals.

Stefan Haacke, Director



## IPCMS News

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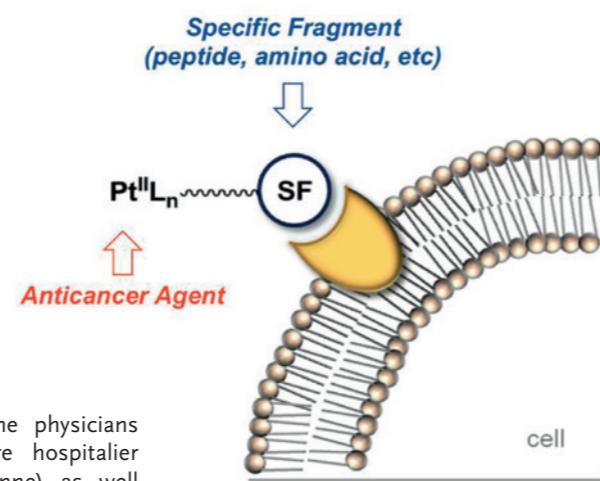
## ♦ Two Biomedical Application Patents

Biomedical inorganic chemistry has become an important area of chemistry in the past half century, and its contributions to medicinal sciences remain numerous, ranging from the development of diagnostic imaging agents to chemotherapeutics. The interface between medicine and inorganic chemistry has been illuminated by the development of cisplatin, one of the most effective anticancer drugs that is used to treat many forms of cancers. Today, however and even though metal-based pharmaceuticals are gaining in importance, progress in selective targeting of cancer cells still needs to be achieved. The effectiveness of cisplatin and its marketed derivatives is limited by severe side effects and by tumor resistance to the drug intrinsically or over time. Our current approach to address these pharmacological issues is to fine-tune the properties of the metal-based agents (mainly platinum) by introducing tailored multifunctional ligands such as N-heterocyclic carbenes (NHC). This possibility to conjugate biomolecules, including amino acids and small synthetic peptides, could be exploited to generate hybrid cytotoxic species linked to cell-directing agents (see Figure).

The results have been protected by two patents, which have recently extended worldwide (PCT application WO2012085479 & WO2012085475). The project involves biologists (Pr S. Fournel, Faculté de Pharmacie, Strasbourg), peptide chemists (Dr G. Guichard, Institut Européen de Chimie et Biologie, Bordeaux), nuclear medicine physicians (Dr A. Clotagatide, Centre hospitalier universitaire de Saint-Etienne) as well as researchers from our Institute (Dr S. Harlepp, Dr E. Chardon, Dr E. Borré and G. Dahm). ■

E. Chardon, G. L. Puleo, G. Dahm, G. Guichard, and S. Bellemain-Laponnaz, *Chemical Communications*, 2011, **47**, 5864–6.

E. Chardon, G. L. Puleo, G. Dahm, S. Fournel, G. Guichard, and S. Bellemain-Laponnaz, *ChemPlusChem*, 2012, **77**, 1028–1038.



E. Chardon, G. Dahm, G. Guichard, and S. Bellemain-Laponnaz, *Organometallics*, 2012, **31**, 7618–7621.

E. Chardon, G. Dahm, G. Guichard, and S. Bellemain-Laponnaz, *Chemistry, an Asian journal*, 2013, **8**, 1232–42.

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## ♦ Whispering galleries for electrons

In "A journey to the center of the earth" published in 1864 [1], Jules Verne's heroes finds his way back thanks to the voices of his companions propagated over long distances along the walls of a natural geological gallery. This intriguing acoustic phenomenon, called "whispering gallery effect", was interpreted half a century later

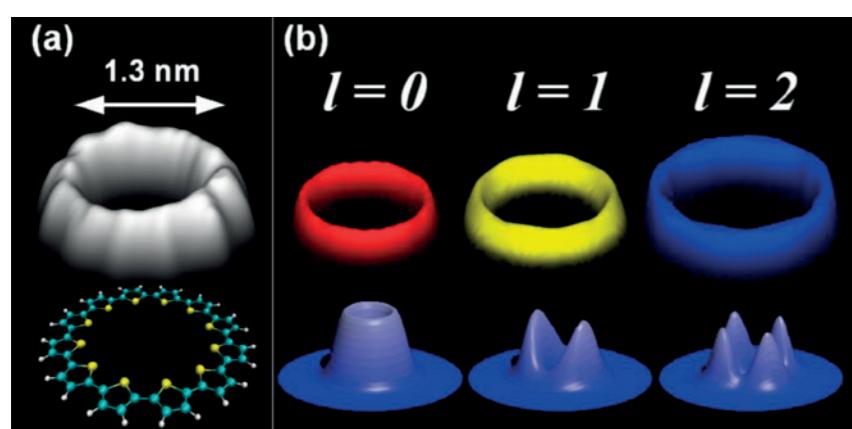
by the physicist Lord Rayleigh who studied the flickers of a candle-flame located close to the walls of the dome of St Paul's Cathedral in London [2].

Later, this phenomenon has been evidenced for other types of waves (optical, radio frequency, etc.). Recently, a team

from the "Institut de Physique et Chimie des Matériaux de Strasbourg" has discovered that the whispering gallery concept could be applied to electrons [3]. These specific galleries must satisfy several conditions: they must be curved, electron conductive and of nanometer size.

In collaboration with a chemist from the "Laboratoire de Chimie des Polymères de l'Université Pierre et Marie Curie (Paris 6)", the CNRS team has synthesized nano-rings of  $\pi$ -conjugated polymers on a gold surface (fig.(a)).

Using a scanning tunnelling microscope (STM) working at cryogenic temperature, the researchers have studied the repartition of the electronic waves in the nano-rings. They discovered that centrifugal forces repel the electrons towards the external border of the cyclic structures. These forces, whose origin is correlated to the curved shape of the structure, are of



▲ (a) STM images and model of an oligothiophene nano-ring. (b) Electronic whispering gallery modes  $l = 0, 1$  and  $2$  of the ring: experiment (top) and theory (bottom).

the same nature than those which allows acoustic waves to propagate along the walls of some monuments: it is a "whispering gallery effect".

In a near future, the researchers will try to "couple" such nano-galleries to each other. In this case, the electrons would be able to jump from one gallery to another. Thanks

to the quantum character of these objects, new methods to transport electric current at the nano-scale will be accessible. ■

[1] Jules Verne, "A journey to the center of the earth", 1864.

[2] Lord Rayleigh, Philos. Mag. **20**, 1001–1004 (1910).

[3] G. Reecht, H. Bulou, F. Scheurer, V. Speisser, B. Carrière, F. Mathevet, and G. Schull, *Physical Review Letters*, 2013, **110**, 056802.

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**IPCMS News**

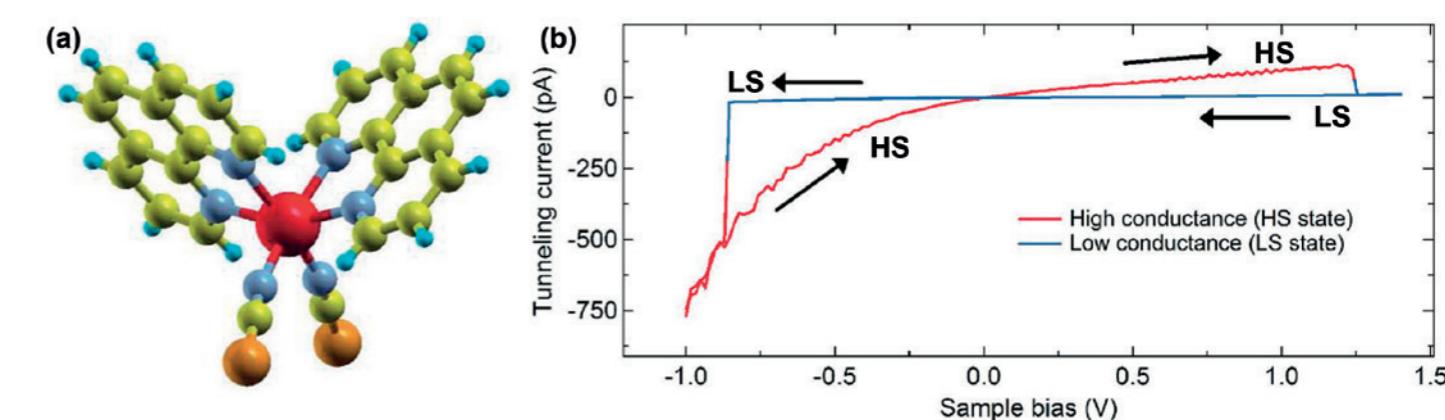
## ♦ Coding a bit of information on a single molecule

Miniaturizing electronic components to the molecular scale is the ambition of molecular electronics. In this domain, researchers from the IPCMS have provided an additional key building block. Within an international collaboration, they managed to deposit, onto a copper substrate, a molecule that is capable of adopting, in a stable manner, two states: one with magnetic properties (high-spin, or HS) and the other without (low-spin, or LS). This molecule can thus store a bit of information: the magnetic state represents a 1 and the non-magnetic state a 0.

This opens interesting perspectives because the present storage technology is close to its limits. Indeed, within our hard disk drives, the physical medium for one bit of information is made up of millions of atoms. Yet, when the bit size is reduced, there appears a phenomenon called superparamagnetism: the bit's magnetic state may spontaneously flip from one state to the other, which impairs any memory applications.

Industrial applications of such a memory device are certainly not around the corner. Indeed, one needs for example to precisely position millions of these molecules on a surface and to interconnect them, for instance using molecular wires. Nevertheless, this work, published in *Nature Communications* in July 2012, prove the validity of the concept. In this respect, the track of metal-organic molecules could prove to be quite fertile. ■

- ▼ (a) The  $\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2$  is used to encode information.  
(b) The current-voltage trace acquired a top a molecule reveals two branches as the molecule is reversibly switched, in a deterministic manner using an electric current, between the HS- and the LS-states.



## ♦ Mechanistic Origin of Vibrational Coherence in Biomimetic Photoswitches

Cis-trans (Z-E) photoisomerization is a mechanism which converts light energy into mechanical energy at the molecular scale. Photoisomerizing molecules may thus be used as building blocks for designing artificial, light-powered molecular motors, or molecular photoswitches used to turn on or off some functionality at the molecular scale. Natural photoreceptors such as the rhodopsin (Rh) protein (the vision pigment) provide examples of very efficient photomechanical energy conversion at the molecular scale. In Rh in particular, the biological function is triggered by the ultrafast, very efficient and vibrationally coherent photoisomerization of retinal. The latter property is remarkable and of special interest in the view of efficient photomechanical energy conversion. Indeed in condensed phase (e.g. in solution) the light energy captured in the electronic excited state of a molecule is very rapidly dissipated into the very large number of vibrational degrees of freedom of the entire system (molecule + thermal bath). Hence, most photoreactions are driven by thermal energy activation from the vibrationally relaxed excited state to the photoproduct state. Conversely, in the vibrationally coherent photoreaction observed in Rh, a significant portion of the photon energy is converted coherently into mechanical energy deliv-

ered in a few specific vibrational modes which drive the photoproduct formation, on a time scale shorter than energy dissipation to the thermal bath.

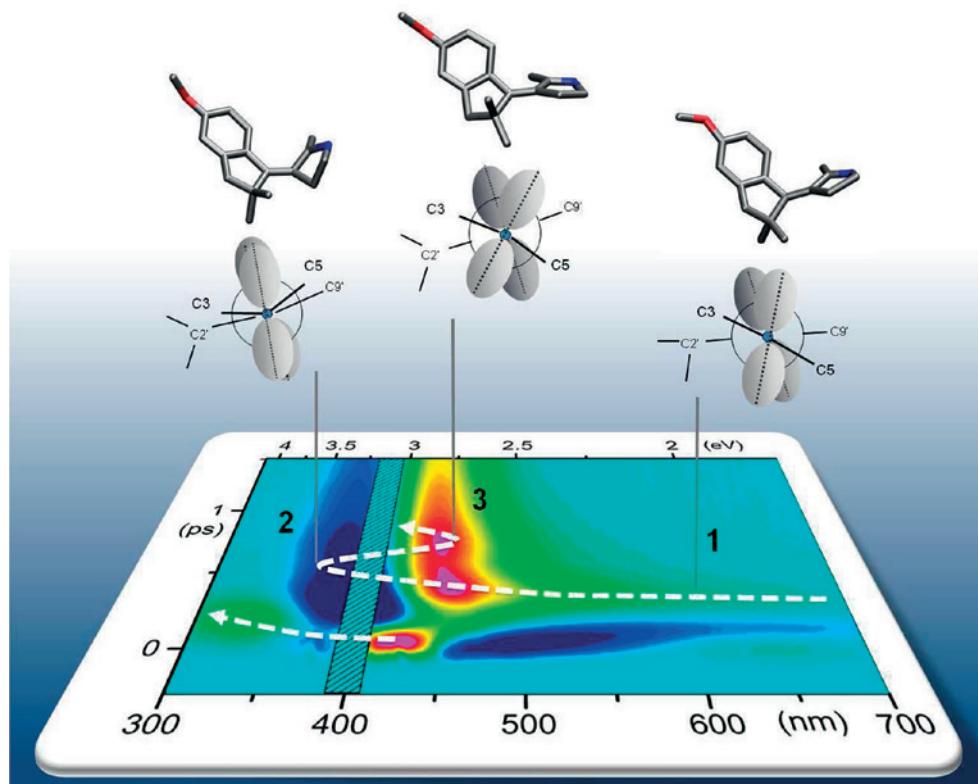
In this context, we investigate the photoisomerization dynamics of synthetic molecular photoswitches, the electronic structures of which have been designed (by computational chemistry) to mimick the excited-state potential energy of retinal in Rh. The goal is to reproduce this outstanding photoreaction, in the view of using the biomimetic system as an efficient molecular switch or motor. Remarkably, the biomimetic systems do reproduce a similarly fast photoreaction and the onset of vibrational coherence which had never been observed in any other photoisomerizing molecule but Rh. In our latest paper on this topic [1], we have extended our experimental findings with the theoretical investigation of a realistic model system imbedded in the solvent. Semi-classical trajectories are computed to model the photoreaction dynamics of the molecules from the excited state to the photoproduct, and spectroscopic signatures of the molecule can be computed along the trajectory. As a result, the low frequency oscillations observed experimentally after the decay to the electronic ground state can be attributed to

structural deformations (in particular ring inversions) which appear to be triggered during the early dynamics in the excited state.

Further combined experimental and theoretical work is in progress at IPCMS and Laboratoire de Chimie Quantique (UdS), in order to unravel the relation between the photoreaction dynamics, the onset of vibrational coherence, and the quantum yield of the photoreaction. One major objective of this research effort is to understand the underlying mechanism that governs the photoreaction dynamics and yield in these artificial molecular switches, and to try and optimize the photoreaction properties either by chemical design or by light excitation. ■

J. Léonard, I. Schapiro, J. Briand, S. Fusi, R. R. Paccani, M. Olivucci, and S. Haacke, *Chemistry - A European Journal*, 2012, **18**, 15296–304.

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◀ Combined experimental and theoretical investigation of the MeO-NAIP molecule in solution allows us to attribute the experimental signatures of vibrational coherences to structural deformation involving in particular ring inversions. The 2D MAP displays the spectrally-resolved transient absorption data in false color, as a function of time delay after light excitation. The dashed, white lines underline dynamic spectral shifts and oscillating signals indicative of vibrational coherence. Semi-classical trajectory modeling allows us to assign these time-dependent spectroscopic features to vibrational dynamics (molecular structures above) causing the modulation of pi-orbital overlaps (Newman projections) hence of the molecule absorption energy and oscillator strength.

## Novel quantum phenomena in strongly interacting dipolar gases

The realization of Bose Einstein condensates (BEC) and quantum degenerate Fermi gases with cold atoms have been highlights of quantum physics during the last decade. Cold atoms in the tens of nanokelvin range are now routinely obtained in the labs, where for high-enough densities ( $\sim 10^{12} \text{ cm}^3$ ), the atomic de Broglie wavelength becomes larger than the typical interparticle distance and quantum statistics governs the many-body dynamics. Characteristic features of the physics of cold atomic gases are the microscopic knowledge of the many-body Hamiltonians which are realized in the experiments and the possibility of controlling and tuning system parameters via external fields. For example, tuning contact interactions by varying the scattering length via Feshbach resonances has already opened the door to the implementation of precise simulations of complex quantum mechanical systems, such as the physics of Bose- and Fermi-Hubbard models.

Breakthroughs in the experimental realization of quantum gases of atoms with a comparatively large magnetic dipole moment (such as  $^{52}\text{Cr}$ ,  $^{168}\text{Er}$  and  $^{164}\text{Dy}$  atoms with dipole moments of up to 10 Bohr's magnetons), and the recent astounding progress in experiments with ultracold heteronuclear polar molecules have now stimulated interest in the properties of low temperature systems with dominant dipolar interactions. Dipole-dipole interactions are

long-ranged, decaying as  $\sim 1/r^3$ , and are anisotropic - the strength and sign of the interaction depends on the relative position of the particles - Compared to cold atoms with contact interactions, these features hold considerable promise in terms of flexibility in realizing novel quantum phases, quantum simulations and even faster gates for quantum computing. The theoretical group of Prof. Guido Pupillo at IPCMS is interested in the development of techniques for the external-field control and modification of interactions between dipolar atoms and molecules as well as on the study of many-body phenomena emerging in these novel quantum systems.

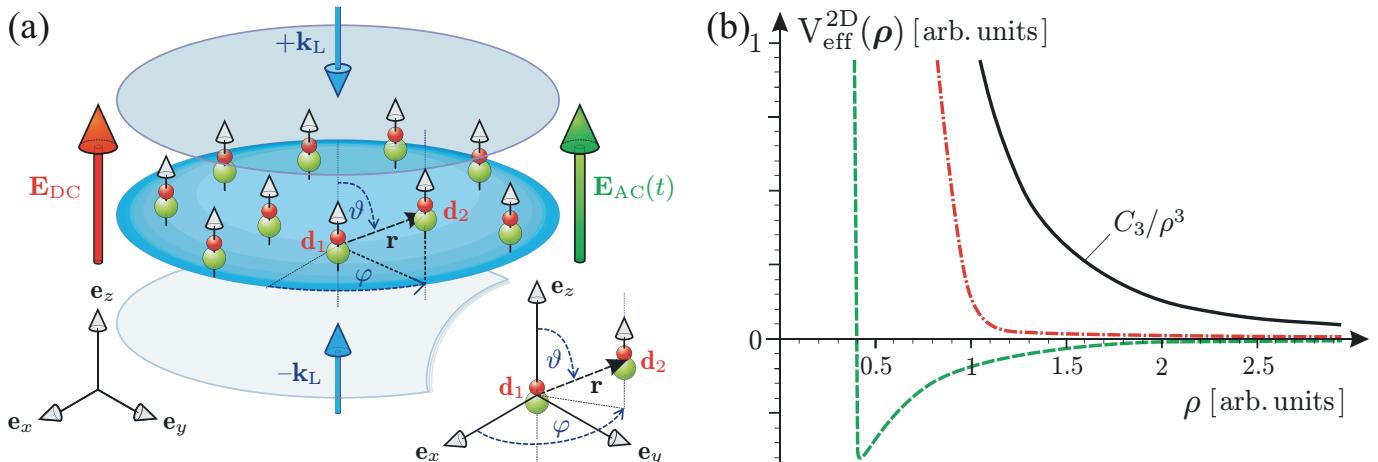
One example is given by gases of heteronuclear bi-alkali polar molecules such as KRb molecules that can now be prepared at sub-micro Kelvin temperatures in the absolute internal electronic, vibrational and rotational groundstate. In the presence of an external electric field mixing rotational excitations, the molecules can be oriented in the laboratory frame and the induced dipole moment can approach its asymptotic value (usually between 0.1 and 10 Debye), corresponding to the permanent dipole moment. This effect can be used to tune the strength of the dipole-dipole interaction. Additional microwave fields allow for advanced tailoring of the interactions between the molecules, where even the shape of interaction potentials can be tuned, in addition to the strength [see figure].

Tunability of interactions forms the basis for the realization of novel quantum phenomena in these systems in the strongly interacting limit, one example being the realization of lattice spin models (a first step in this direction has been recently achieved experimentally using KRb polar molecules [1]). As a result of this progress, in the last few years dipolar gases have become the subject of intensive theoretical efforts, and there is now an extensive body of literature predicting novel properties for these systems. A recent summary of these works can be found for example in [2], where the focus is on the demonstration of connections and differences between dipolar gaseous systems and traditional condensed-matter systems, and on the inherent interdisciplinary nature of these studies. ■

[1] B. Yan, S. A. Moses, B. Gadway, J. P. Covey, K. R. A. Hazzard, A. M. Rey, D. S. Jin, J. Ye, arXiv:1305.5598.

[2] M. Baranov, M. Dalmonte, G. Pupillo, P. Zoller, *Chemical Reviews*, (2012) **112**, 5012-61.

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(a) Polar molecules are trapped in the  $(x; y)$ -plane by an optical lattice made of two counter-propagating laser beams with wavevectors  $\pm k_L$  (blue arrows). The dipoles are aligned in the  $z$ -direction by a DC electric field  $E_{DC}$  (red arrow). An AC microwave field is indicated (green arrow). Inset: Definition of polar ( $\theta$ ) and azimuthal ( $\varphi$ ) angles for the relative orientation of the inter-molecular collision axis with respect to a space-fixed frame, with axis along  $z$ . (b) Sketch of effective 2D potentials  $V_{\text{eff}}^{2D}$  for polar molecules confined in the 2D (pancake) geometry of panel (a). Characteristic ranges of molecular interactions are of 10-100 nm, much larger than the molecular core. [Figure adapted from [2]].