

Alkwin Slenczka and Bretislav Friedrich provide insight into their joint project on solvation and cluster formation in helium nanodroplets



Alkwin Slenczka



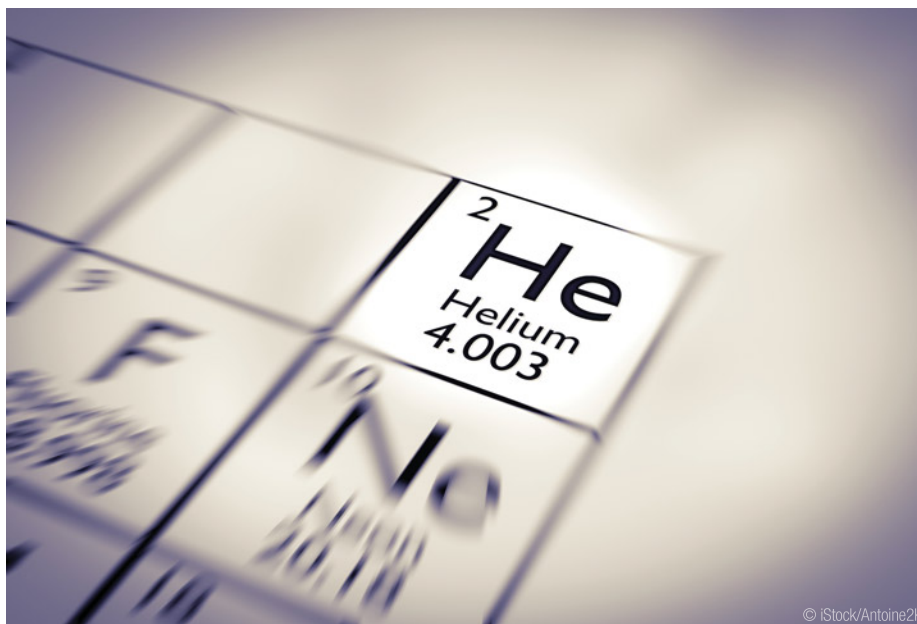
Bretislav Friedrich

Solvation and cluster formation in helium nanodroplets

In vacuum, a molecule is free to exercise its quantum motions: it can vibrate and tumble as well as undulate along as a whole (as a de Broglie wave). But what happens when a molecule enters a liquid, in particular a superfluid liquid such as liquid helium?

Upon entering a liquid host, the molecular motions are characteristically modified, depending on the interactions involved. The molecule will undergo multiple scattering by the liquid's constituent atoms or molecules and eventually end up in equilibrium with the liquid. The equilibration entails thermalisation of the molecule's vibration, rotation and translation to the liquid's temperature as well as solvation of the molecule by the liquid's constituents, whereby the molecule becomes a solute and the liquid a solvent. In the absence of a chemical reaction, the solvation, i.e., the sticking of the solvent to the solute, is due to van der Waals forces. These arise from the interactions between the electric dipoles – permanent or induced – of the solute with the solvent. The resulting aggregates of the solute and the solvent are termed 'van der Waals complexes'. Upon their formation, they remain embedded in the solvent.

The most general – and simultaneously the weakest – variety of van der Waals forces are the London dispersion forces. First invoked in 1930 by Fritz London, dispersion forces are a necessary consequence of the quantum electron correlations that govern the induced dipole-induced dipole attraction between atoms or nonpolar molecules at large separations. Proportional to polarisability, London dispersion forces are especially weak for rare gas atoms, which shun entering into unions with other like or unlike atoms or molecules as a result. Reluctantly, dispersion forces are behind the condensation of



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rare gases and give rise to supramolecular structures and to physisorption.

Since the binding energy of van der Waals complexes held together by dispersion forces amounts to fractions of Kelvins (energy divided by Boltzmann's constant), the study of such complexes must proceed at correspondingly low energies/temperatures. At the same time, these sub-Kelvin conditions are befitting high-resolution spectroscopy, which is, therefore, the technique of choice for probing such complexes – and thereby solvation by sub-Kelvin liquids.

Helium nanodroplets

Which species remains liquid when cooled to sub-Kelvin temperatures? Due to the tight binding of its electrons – and consequently tiny polarizability – it is only helium that keeps clear from becoming a solid and remains a liquid upon

condensation down to the zero point of temperature at pressures below 25 bar. Moreover, depending on the isotope, helium forms a superfluid, i.e., a special state of a liquid entered below a critical temperature, which is characterised by vanishing viscosity and high heat conductivity. The common (bosonic) isotope, ^4He , becomes superfluid at 2.17 K as a consequence of the Bose-Einstein condensation of its atoms into their macroscopic quantum ground state.

It was realized by Peter Toennies in the 1980s that dissolving molecules in liquid helium could be accomplished in a well-defined manner by making use of freely levitating helium nanodroplets rather than bulk helium held in a thermos. An intense beam – or stream – of such droplets could be generated by expanding helium into a vacuum at the above-mentioned cryogenic conditions and high pressures. Giacinto Scoles,

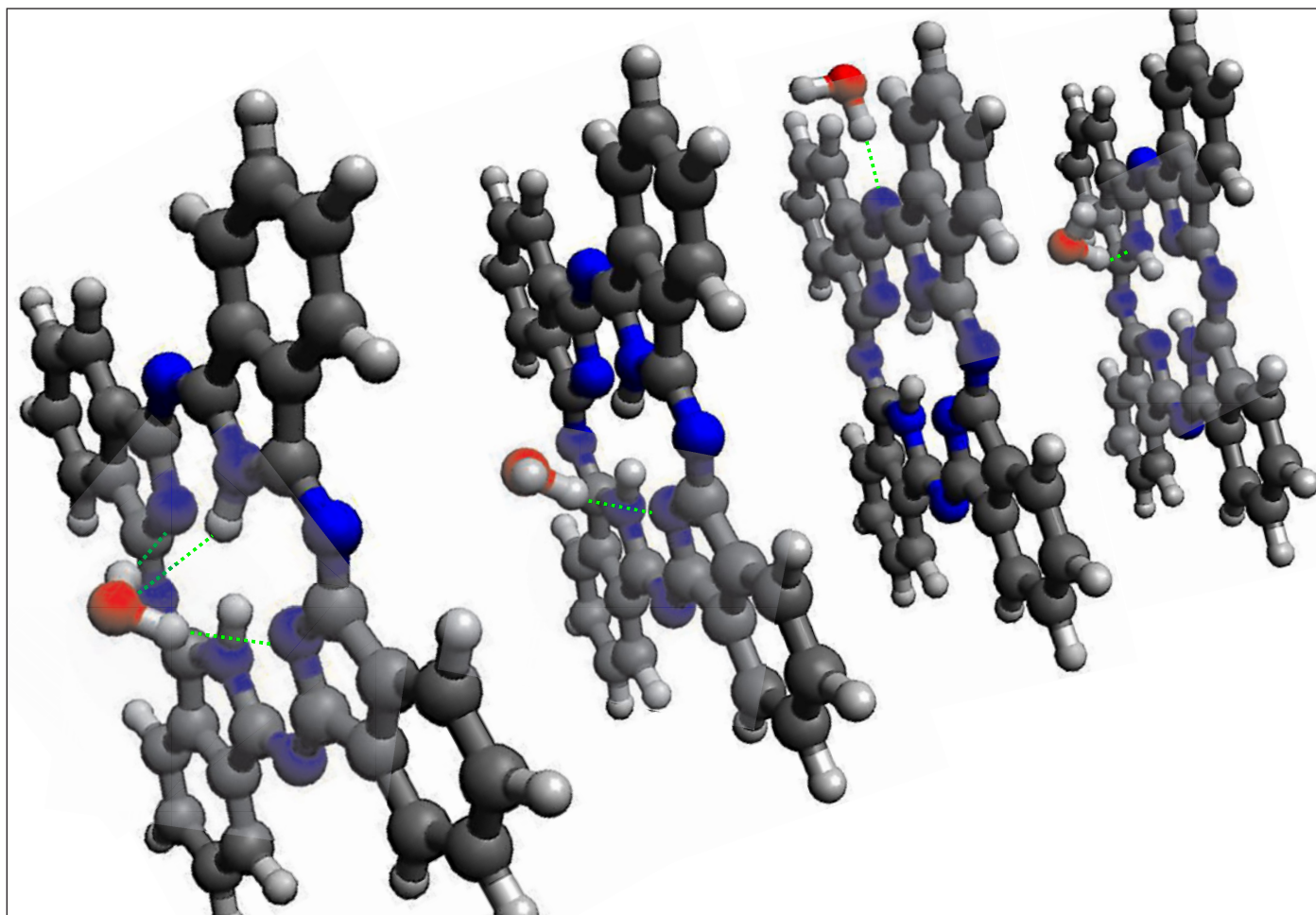


Fig. 1 Different isomeric configurations can already occur for such large organic molecules as phtalocyanine (Pc) aggregated with a single atom or molecule such as water (example above). The four configurations of Pc-H₂O found theoretically are ordered according to their stability (decreasing from bottom left to top right)

as well as Toennies working together with Andrey Vilesov, showed that foreign atoms or molecules and even molecular aggregates could be investigated within the droplets by means of laser spectroscopy. Aimed either at the dopant (solute) species or the helium environment (solvent) or their mutual interaction (solvation), these investigations have been making use of the following features offered by helium droplets.

- The helium droplets produced by expanding helium gas into vacuum at cryogenic temperatures are nanometer-sized with a uniform temperature of 0.38 ± 0.01 K, which is governed by evaporative cooling of helium atoms from the droplets' surface
- By passing the stream of helium droplets through a pick up cell, one or more molecules can be doped into a droplet, depending on the droplet size and the vapor pressure of the molecular species in the cell
- Multiple species can be doped into a given droplet by passage through multiple pick up cells. Since the dopant-to-dopant long-range attractive forces exceed the dopant-to-helium forces, the formation of a molecular complex inside the droplet is ensured as soon as its constituents are captured by the droplet.

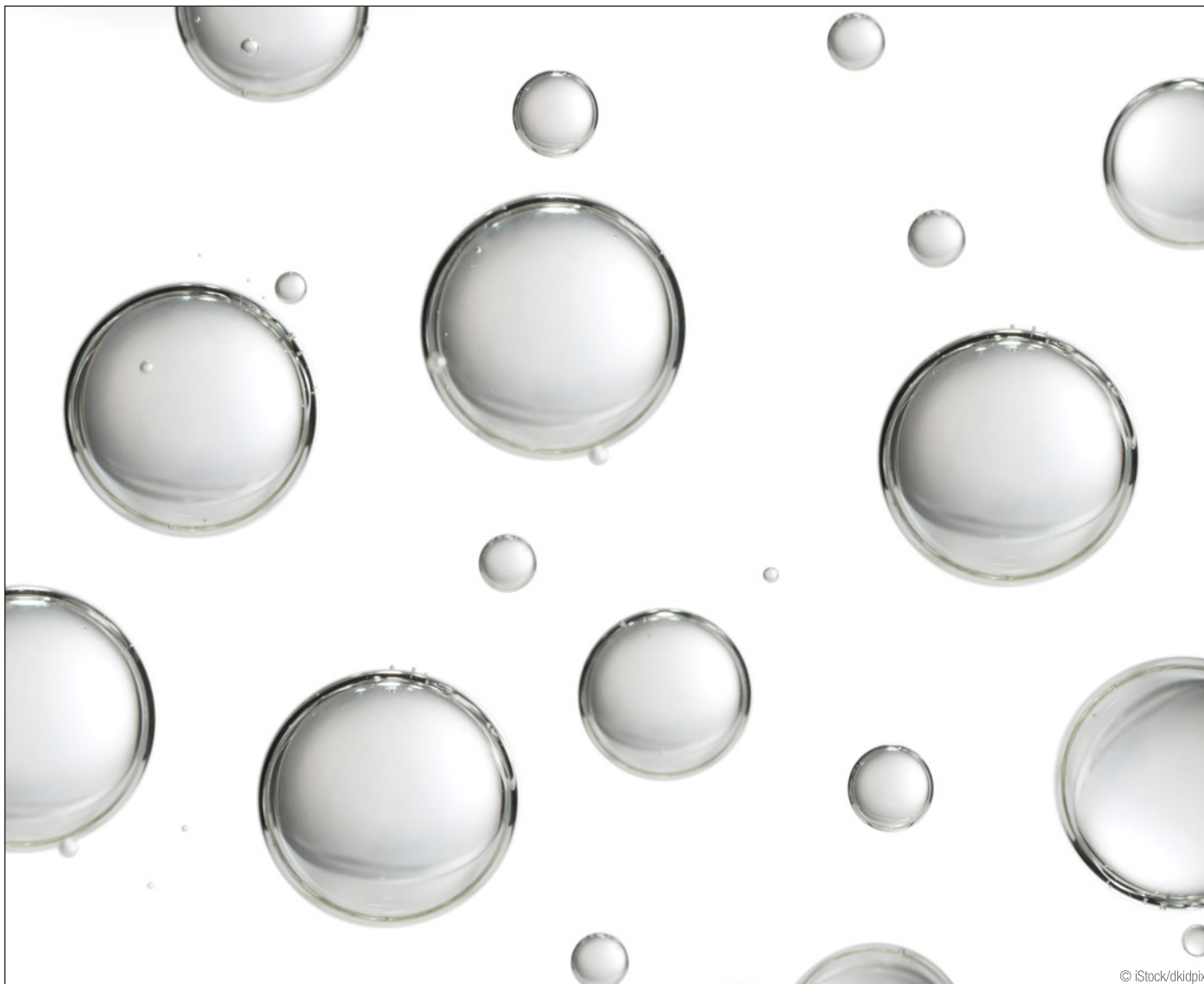
Moreover, compared with complex formation in the gas phase, the helium droplet serves to increase – by orders of magnitude – the effective capture cross section and thus the probability of forming complexes.

The complexes thus 'synthesised' have a well-defined composition and stoichiometry, which can be probed spectroscopically as a function of the vapor pressure in the pick-up cell(s). In contrast to the standard methods of mass spectrometry, this procedure is non-destructive even for the weakest of binding energies. Superfluid helium nanodroplets hence represent an ideal host environment for generating stoichiometrically well-defined and cold van der Waals complexes – and for investigating their solvation.

Building on the previous work by Toennies and others, the Slenczka laboratory at Regensburg devoted its effort to investigating molecules and molecular aggregates with particular emphasis on their microsolvation in helium droplets. The solvated species are probed via high-resolution optical spectroscopy, which brings in not just the electronic ground state of the probed species but also its electronically excited state.

Isomeric variants

Like in the gas phase, a complex with a given stoichiometry can come about in different configurations, termed 'isomeric variants'. The identification of isomeric variants for a particular stoichiometry can be accomplished by investigating dispersed emission spectra. If dissipation of the excess excitation energy takes place, the dispersed emission is comprised exclusively of red-shifted radiation and so there is no emission signal at the excitation energy/frequency. While red-shifted dispersed emission may also appear for other reasons, the observation of dispersed emission whose frequency coincides with the excitation frequency is a clear signature of an electronic origin, which, in turn, identifies a particular configuration of the complex. The observation of more than a single electronic origin from resonances assigned to an identical stoichiometry thus reveals the presence of isomeric variants. As the isomeric variants arise from the intermolecular van der Waals interaction within the complex, their identification provides a valuable insight into binding by these weak forces. In order to gain structural information about the isomeric variants, their nuclear configurations need to be investigated as well.



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Much of the fine structure seen at the electronic origin of the above dopant species is sensitive to variation of the droplet size distribution

For molecules, the superfluid environment of the droplet affords a nearly-free mobility of the dopant species embedded in the droplet, as inferred from a host of rotationally resolved infrared spectra obtained by Toennies and Vilesov as well as by the groups of Roger E. Miller and Garry Douberly. Typically, the spectra of small molecules exhibit features that can be interpreted as arising from the rotation of a rather rigid solvation complex consisting of the dopant molecule with some He atoms rigidly attached to it and hence a correspondingly increased moment of inertia.

Investigations via optical spectroscopy

However, our investigations via optical spectroscopy reveal that the fine structure resolved at the corresponding electronic origin of closed-shell organic dopant molecules such as phtalocyanine, porphine, tetracene, and pentacene is inconsistent with the free rotation of the molecules or their complexes with helium. While deviations of the spectral features termed 'phonon wings' from the spectrum of elementary excitations (phonons) of superfluid helium could be explained by the presence of a non-superfluid

helium solvation layer, the fact of the missing rotational fine structure contradicts the empirical model for microsolvation inside superfluid helium.

Much of the fine structure seen at the electronic origin of the above dopant species is sensitive to variation of the droplet size distribution. Only one particular feature (namely the asymmetric shape of the spectral lines) could be identified as due to the droplet size distribution. Apparently, our current understanding of the helium-induced fine structure in electronic spectra of large organic molecules doped into superfluid He droplets – amounting to microsolvation in superfluid helium – is still rather fragmentary and speculative. It can perhaps be best expressed by the following paraphrase (abridged) of a well-known soliloquy:

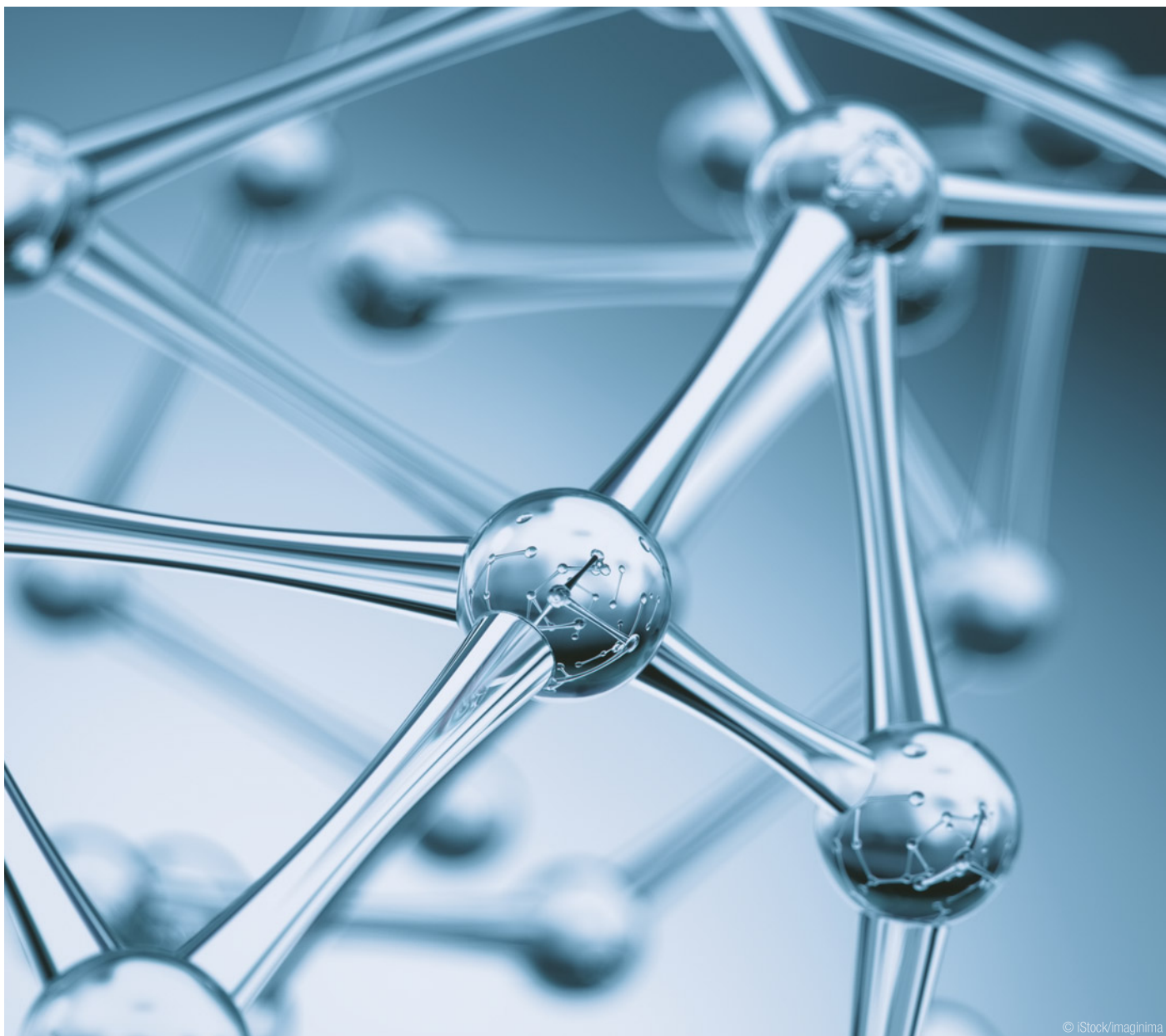
*'To tumble, or not to tumble, that is the question:
Whether 'tis nobler in the bulk to suffer
The wings that arose from phonons' nimble jitter
Or to shuffle off this lubricious coil for ever
And swirl through a void that we know not at all,
An enterprise of great pitch and moment
to enthrall'*

The ultimate step in the analysis of van der Waals complexes

In order to be able to infer structures and make assignments unequivocally, we need more data – and a better understanding. Our future work therefore aims at unraveling the mystery of the missing rotational fine structure by studying polar molecular complexes – in both helium droplets and the gas phase – whose rotation can be controlled by an external electric field. Thereby we will also be able to take the ultimate step in the analysis of van der Waals complexes which goes beyond the identification of the number of isomeric variants, namely to elucidate the intrinsic configuration of each complex.

The role of Stark spectroscopy

The configuration correlates with the mass distribution which, in turn, determines the moment of inertia of the complex. Thus, the measurement of the moment of inertia provides an insight into the configuration of the complex. In our ongoing work, we seek to determine the moments of inertia from Stark spectroscopy, where a static electric



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In their ongoing work, Friedrich and Slenczka seek to determine the moments of inertia and the molecular electric dipole moments from Stark spectroscopy, where a static electric field generates a cosine potential for a dipolar complex

field generates a cosine potential for a dipolar complex. Stark spectra reveal not only the moment of inertia but also the body-fixed permanent dipole moment of the complex, which represents another valuable piece of information about the complex structure and the intermolecular dispersion forces that hold it together.

Although sensitive only to polar complexes, Stark spectroscopy can be also applied to complexes of non-polar molecules which, as a whole, are often polar. Note that such van der Waals complexes are bound exclusively by London dispersion forces. Their spectroscopy-based structural analysis is thus inseparable from examining their microsolvation, which involves London dispersion forces as well.

Non-polar planar organic molecules

On the dopant side, our work is focused on complexes of non-polar planar organic molecules,

such as porphyrines and phthalocyanines with rare gas atoms, such as argon, or small polar molecules, such as water. The surface of a large planar organic molecule provides several sites for the attachment of a single atom or a small molecule, whereby the low-temperature conditions available in superfluid helium droplets promote stabilisation of local-minimum sites – in addition to the global minimum. Thus, different isomeric configurations can already occur for such molecules aggregated with a single atom or molecule, as illustrated in Fig. 1 by the four theoretically predicted configurations of the phthalocyanine-water complex, ordered according to their stability (decreasing from bottom left to top right).

The ability to ‘synthesise’ and probe molecular complexes in superfluid helium droplets provides access to van der Waals complexes including those bound by London dispersion forces and advances our understanding of microsolvation of molecules in a quantum fluid.



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