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Spectroscopy and chemistry of interstellar ice analogues

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CHAPTER 8

Future challenges

Astrophysical laboratory techniques have been and will be of unprecedented value for interpreting and guiding astronomical observations. Spectroscopic data, both in the gas phase and in the solid state, allow to identify species in space and to derive inter- and circumstellar abundances. Experimentally derived rate constants, in addition, serve as input for astrochemical models which can be directly compared to observations. In the last decades, the progress in laboratory based research has boosted the understanding of chemical processes in space. With the further improvement of new upcoming observational facilities and the refinement of chemical models, there is a need for more and more detailed laboratory data. In this chapter experimental challenges are addressed that will be useful for astronomy using *OASIS*, the new setup that has been described here.

In Chapters 5 – 7 it was shown that it is possible to study the photochemistry of PAHs in water ice upon VUV irradiation through optical (i.e. electronic) spectroscopy using direct absorption spectroscopy. The method allows studying reaction products in situ and in real time. As such the technique offers a very versatile and generally applicable tool that is capable of studying other systems as well, both substantially larger and smaller. This provides information needed for identifying species in space as well as insight in possible reaction schemes. The latter point has been addressed in detailed in this thesis, but the use of this work for an astronomical detection of a PAH in the solid state, has only been mentioned in §5.5. The optical PAH ice data, presented in this thesis, basically hold the promise to search for optical solid state PAH signatures in space, as an alternative to electronic gas phase work that has been unsuccessful so far. A kick-off project with the ESO-VLT equipped with the FORS2 spectrometer towards the embedded K0 star DoAr21 has been performed to search for broad absorption features that may be correlated to the absorption bands described for the PAHs and PAH-derivatives in this thesis. The analysis of the data is still in progress and at this stage only the effort to identify PAH in space through their ice spectrum is reported.

It is generally expected that also (and according to several publications, particularly) large PAHs containing 50 carbon atoms or more, the so called GRAND-PAHs, and their photoproducts are present in space. These are expected to be formed in the stellar ejecta of dying stars. Gas phase spectra of such complex PAHs are lacking, mainly because of the experimental challenges that go along with bringing such molecules in the gas phase in the laboratory. The only data available on large PAHs today are from matrix isolation spectroscopy. In such experiments, mainly argon and neon are used as a molecular surrounding, as for such environments matrix interactions are as small as possible. *OASIS* can be used in a similar way, as a regular matrix setup, guiding gas phase studies. Test experiments have been performed on $B_{ghi}P$ ($C_{22}H_{12}$) and hexa-peri-hexabenzocoronene (HBC $C_{42}H_{18}$) using argon instead of water as a matrix. The results are shown in Figure 8.1. The distortion of the PAH energetic structure is proportional to the polarizability of the matrix material. If the purpose of the experiments would be to measure the energy of free PAH molecules, i.e. gas phase species, the experiments are to be performed for more than one matrix material. One could for example measure the spectra in xenon, argon and neon. If the transition energies are now plotted as a function of polarizability of the matrix, it is possible to extrapolate the energy level to zero polarizability, i.e. the electronic energy in vacuum. This is a good indication of the origin of gas phase electronic transitions. This method, subsequently, can be employed to select (GRAND-)PAHs which possibly contribute to diffuse interstellar band absorption features.

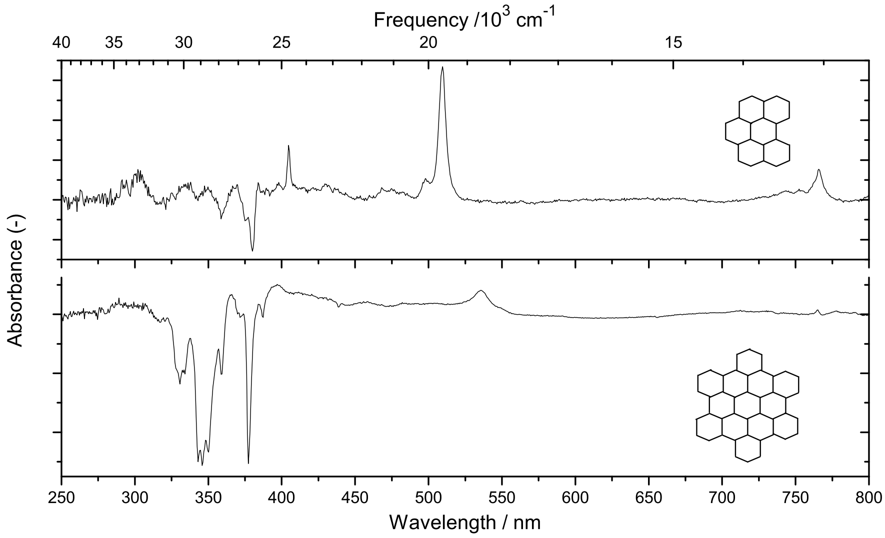

Figure 8.1 The spectrum of matrix isolated Hexa-peri-benzo-coronene and its cation in argon at 12 K (bottom) plotted together with matrix isolated benzo[ghi]perylene and its cation band in argon at 12 K (top)

The general applicability of *OASIS* is also demonstrated with a set of test measurements on a different type of carbon containing molecules, the nano-diamonds adamantane ($C_{10}H_{16}$) and diamantane ($C_{14}H_{20}$). The species are abundantly present in meteorites and are thought to exist in other regions of the interstellar medium as well. Calculations predict that these species are easily ionized by Lyman-alpha radiation and that their cationic species have moderately strong electronic transitions in the optical part of the electromagnetic spectrum [M. Steglich, priv. comm.]. Again, a possibility exists that such species contribute to absorptions in the diffuse interstellar medium. The test measurements performed so far, were done in high concentration matrices and did not exhibit absorption bands that originate from diamondoid ions. Further work is needed.

The next step is to include 'real' prebiotical molecules in the ice. In the last year it was shown that VUV irradiation of a pure methanol ice results in the generation of more complex species such as ethanol, methylformate, acetic acid, glycol aldehyde and ethylene glycol [Öberg et al. 2009c]. That study was based on a long research tradition in Leiden and follows the experiments by Greenberg and coworkers who irradiated astronomical ice equivalents with a VUV broadband light source for many days and identified gas chromatographically amino acids in the resulting organic refractory [Muñoz Caro et al. 2002]. Even though the experiments were performed under quite rough experimental conditions (the residue had to be analyzed outside the vacuum and after warm-up) this has set the tone for this field. An alternative way for this bottom-up approach is a top-down scenario in which the focus is not on the generation of more complex species, starting from simple precursors, but to include real biological systems — e.g. nucleobases, ribonucleotides and their biosynthesis precursors — in the ice and to study their photostability. This can be ideally studied with the new experimental setup and will be a research topic in the next years.

Another interesting subject that can be addressed with *OASIS* is that of the production of small radicals in interstellar ices. In Chapter 6, for example, the observation of $HCO^{\cdot}$ is reported. OH is another interesting object, as the production rate of OH radicals in an interstellar water ice is not yet fully understood. As infrared techniques are generally slow, such methods are not suited to address this question, and the optical equivalent described here offers an alternative. The first test measurements on irradiated pure H_2O ices show that some new very broad absorptions indeed present. This is overcome by doping an argon matrix with H_2O, with a resulting concentration of about 1:100 (H_2O:Ar). A vibronic progression ascribed to the $A^2\Sigma^+(v{=}0) \leftarrow X^2\Pi_{3/2}(v{=}0)$ transition at 308 nm is found [Hancock & Kasyutich 2004]. These test measurements can be extended to more astronomically relevant ices. Ultimately, the diffusion of radical species in the matrix can be studies as a function of temperature.

Finally, *OASIS* was initially designed as *CESSS*: a Cavity Enhanced Solid State Spectrometer. The setup is equipped with two stable and micrometer adjustable mirror mounts on the in and outlet port of the vacuum system. The initial idea was to use an incoherent broad band cavity enhanced detection scheme [Fiedler et al. 2003] to perform the experiments that have been described in this thesis. This did not work in the solid state, presumably because of the light refraction in the ice. Fortunately, a singly pass experiment turned out to be sensitive enough. In the gas phase, however, the system works fine.

A set of mirrors with reflectivities as high as 99.95% can be aligned perpendicular by a HeNe laser. The resulting system behaves like a cavity, which can be excited by intense broad band white light originating from the Xe-lamp. Light will continuously leak out of exit side of the cavity. This light has traversed through the cavity for some time, depending on the reflectivity of the mirrors, resulting in an enhancement of the absorption

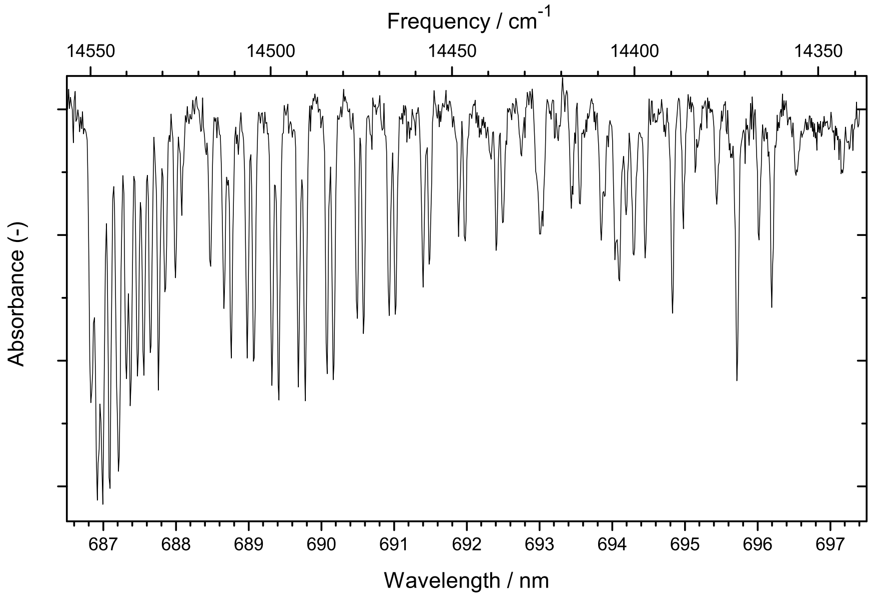

Figure 8.2 The absorption spectrum of the $b^1\Sigma_g^+(\nu{=}1)\leftarrow X^3\Sigma_g^-(\nu{=}0)$ oxygen transition

path length, which directly reflects the increase in sensitivity of the detection technique [Fiedler et al. 2003]. The power of this arrangement is exemplified by a spectroscopic measurement on the doubly forbidden The forbidden $b^1\Sigma_g^+(\nu{=}1)\leftarrow X^3\Sigma_g^-(\nu{=}0)$ gas phase oxygen transition can only be observed in the 50 cm long absorption cell, if significant enhancement is achieved in the cavity [O'Keefe & Deacon 1988]. A typical absorption spectrum taken under atmospheric pressure is shown in Fig. 8.2. The example indicates the power of the setup for performing spectroscopic studies on gas phase species. Of course, this technique can be used for measurements on astrophysically relevant species. With minor adjustment of the system, one can sensitively perform spectroscopy on a (plasma) expansion over a large frequency range with moderately high resolution.

In conclusion, *OASIS* has turned out to be a very versatile tool that has proven its use for astronomical research.