PART V

THE DIB CARRIER CANDIDATES

Solid State DIBs

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Abstract. The diffuse interstellar bands are not due to solid state species. However, under the explicit assumption that DIB carriers survive the transfer from translucent to dark clouds, it is expected that for the low temperatures in the dense interstellar medium also DIB carriers accrete onto dust grains. Like all other molecules, apart from molecular hydrogen, they will get embedded in an ice matrix that largely consists of amorphous solid water. This offers - in principle - a tool to search for DIBs in complete different environments, both in space (i.e., towards embedded young stellar objects) and in the laboratory, namely in the solid state simulating interstellar ice analogues. Currently experiments are ongoing in the Sackler Laboratory for Astrophysics at Leiden Observatory to record optical ice spectra of potential DIB carriers. For this a new experimental approach has been developed. Its performance and potential are discussed.

Keywords. methods: laboratory, ISM: molecules, molecular data,

1. Introduction

Rare gas matrix spectra of possible DIB carriers have been very useful in providing approximate wavelengths for the corresponding gas phase data (e.g. Nagarajan & Maier 2010). A direct comparison between matrix spectra and DIBs, however, is not useful as matrix interactions induce shifts that in the ultra-violet-visibile (UV-VIS) can exceed tens of wavenumbers. Still, solid state spectra may be helpful in identifying DIB carriers, following recent observational (Öberg *et al.* 2011) and laboratory based progress (Allodi *et al.* 2013) in the field of inter- and circumstellar ice research.

In the diffuse medium grains are barely covered by molecules. The relative high temperatures and intense radiation fields induce thermal and photo-desorption prohibiting the growth of multi-monolayers thick ices. However, upon gravitational collapse and darkening of the cloud, temperatures drop and dust grains start acting as micrometer sized cryopumps. Different species accrete sequentially, until even the most volatile species are frozen. Observations with ISO and Spitzer (Gibb *et al.* 2004, Öberg 2011) show that a number of compounds - particularly CO_2, CO, CH_3OH, NH_3 and CH_4 - are embedded, largely in amorphous solid water (ASW), intimately mixed, or as layers on top, depending on a number of physical-chemical parameters that govern accretion, (non)thermal desorption, segregation and solid state chemistry (Linnartz *et al.* 2010). The latter is triggered by (non)energetic processes that take place - irradiation by Ly-α photons from cosmic rays excited H_2, impacting H-, D-, C-, N-, O-atoms, highly charged ions or free electrons - particularly during planet and star formation when radiation and particle fluxes are intense. Under these conditions interstellar ices provide a molecule sink where molecules may interact and react.

The goal of this short contribution is to discuss the possibility to search for optical spectra of interstellar ices and to link these to the diffuse interstellar band problem. From an observational point of view such data are largely lacking; the majority of the ice studies

have been made in the infrared where vibrational modes are used for an identification. Most laboratory work of interstellar ice constituents so far is also restricted to the infrared and characterizes vibrational parameters; band position, bandwidth, and band intensity (see e.g. Bernstein *et al.* 2007). An extension to the UV-VIS and near-infrared (IR) allows to monitor electronic properties of interstellar ice analogues (Gudipati & Allamandola 2003, 2006; Bouwman *et al.* 2009, 2010; Cuylle *et al.* 2012). Such studies have several advantages that may be particularly interesting within the context of DIB research; 1) the main ice components do not (strongly) absorb in the optical range, 2) optical (i.e., electronic) spectra are more unique than in the IR where comparable vibrational modes of different molecules yield similar spectra, and 3) the optical transition strengths are generally much higher, allowing to study highly dilute i.e., astronomically realistic ice mixtures (Cuylle *et al.* 2013). Below a new experimental concept for DIB research is introduced. Pros and cons are discussed. Its performance is demonstrated on the example of frozen PAH-cations. PAH cations have been and still are considered as possible DIB carriers (see elsewhere in these proceedings).

2. Experimental

Our experimental setup OASIS (Optical Absorption Setup for Ice Spectroscopy) utilizes incoherent, broadband, direct absorption spectroscopy. The full experimental details are available from Bouwman *et al.* (2009) and Allodi *et al.* (2013). OASIS comprises a central high vacuum chamber (about 10^{-7} mbar) on top of which a turnable closed cycle helium refrigerator is mounted. A MgF sample window is connected to the cold finger and temperatures can be regulated between 12 and 325 K using resistive heating. Ices are grown by vapour deposition of purified gases. Solid (PAH) precursor material is deposited together with the matrix material using small ovens. The flow rate of the matrix material is accurately set by a high precision dosing valve, while the evaporation rate of the solid precursor can be roughly chosen by changing the power of the heater. Condensation at any place inside the tube is prohibited by additional resistive heating along the full length of the deposition tube. The growing ice film thickness is accurately measured by recording in parallel the number of interference fringe maxima of a HeNe laser beam reflected from the ice and absolute concentrations are subsequently deduced from a correlation of the measured absorption strengths.

The UV-VIS spectra are recorded by focussing broad band (200 nm – 1 μm) light of a 150 W Xe arc lamp through the ice, along the optical axis, coinciding with the HeNe beam. Light that is not absorbed in the ice is focussed onto the entrance slit of a spectrometer (Shamrock 303i). This spectrometer is equipped with two interchangeable turrets which hold four gratings in total (2400, 1200, 600 and 150 l/mm), allowing for a trade-off between wavelength coverage and spectral resolution, depending on experimental needs. For solid state DIBs, obviously, high resolution is not needed and a 150 l/mm grating is more than sufficient, allowing total wavelengths coverages up to 150 nm with a band width of the order of 4 nm. The light is subsequently dispersed onto a very sensitive 1024x256 pixel CCD camera with 16 bit digitization (ANDOR iDus DV-420 OE). The resulting signal is read out in vertical binning mode by a data acquisition computer. Spectra are taken in absorbance with respect to a reference spectrum that is taken directly after sample deposition. The recording of a single spectrum takes about 10 s and typically consists of 100 spectra co-added to improve S/N ratios. In a regular experiment more than 1000 individual spectra are recorded and reduced using LabView routines.

To trigger also reactions in the ice, the PAH:H_2O ices are irradiated by UV radiation from a microwave powered H_2 discharge lamp that simulates the Ly-α emission pattern typical for the interstellar radiation field in the dense ISM upon cosmic ray excitation of molecular hydrogen. The lamp is centred on the front flange and directed towards the ice. Typical UV fluxes amount to 5×10^{13} photons cm^{-2} s^{-1}. Spectra are subsequently subtracted from the unprocessed ice spectrum, yielding a difference spectrum in which negative signals indicate that a precursor species is consumed, and positive signals correspond to the formation of a new species. For the data reduction local linear baseline corrections and multiple Gaussian fitting of the band profiles are applied. As the HeNe laser and visible absorption spectrum are monitored simultaneously, these measurements can be performed with full characterization of the ice composition. Hence, the setup allows high quality, sub-second time resolution spectroscopic experiments in which the photoprocessing of well-defined interstellar ice analogues can be carefully monitored.

This makes OASIS ideally suited for ice research in a wavelength domain in which observational astronomy has been historically strong. Below results are presented for solid state PAH (cations), embedded in amorphous solid water.

3. Results and discussion

In Figure 1 the UV-VIS spectra are shown for four different (commercially available) PAHs - Anthracene (Ant, $C_{14}H_{10}$), Pyrene (Py, $C_{16}H_{10}$), Benzo[ghi]perylene ($B_{ghi}P$, $C_{22}H_{12}$) and Coronene (Cor, $C_{24}H_{12}$) embedded in amorphous solid water and upon Ly-α irradiation (see Bouwman *et al.* 2011). Typical PAH:H_2O mixing ratios range from 1:1000 to 1:10000. Even more diluted mixtures (H_2O:Cor = 1:30000) result in still detectable (single pass) signals. Such mixing ratios are comparable to the predicted ISM ice values, where overall (i.e., cumulative) PAH abundances of the order of a few percent are assumed.

In the previous studies, listed above, the solid state dynamics of vacuum UV irradiated PAHs in water ice have been discussed. The focus here is on the spectroscopic features that are deduced. The neutral PAH bands cover typical the high energy range of the UV-VIS, i.e., below 350 nm, and are not expected to be of direct DIB interest. Their solid state assignments can be easily made following rare gas matrix studies, even though the water environment causes bands to shift and broaden more, mainly because of the stronger molecular interactions in a polar environment. The latter is also true for the majority of the reaction products, mainly PAH-cation features, as the ionisation channel dominates for the low PAH abundances used here (Cuylle *et al.* 2013). Their absorption features, however, overlap with the wavelength region in which DIBs are found. A comparison of the four spectra shows that even with broadening the electronic PAH-cation spectra are sufficiently different to discriminate for individual species. Whereas in the IR the typical PAH CH stretches and in/out-of-plane bending motions coincide for individual species, in the UV-VIS the different electronic properties are reflected by clearly different spectra. In principle this provides a solid state route for identifying new species in space. It should be noted though, that adding more and more different PAHs to the ice, likely results in overlapping spectra as well. Also, one should recall that several gas phase spectra of PAH-cations did not result in convincing matches between laboratory and astronomical data (see elsewhere in these proceedings). Actually, an unambiguous identification of a specific PAH is still lacking and their likely presence in space is mainly deduced through their UV pumped IR emission features in the 3.3 - 18 μm region (e.g. Tielens 2008). Therefore, a solid state identification - with or without a direct link to DIBs - would be already an important achievement on its own.
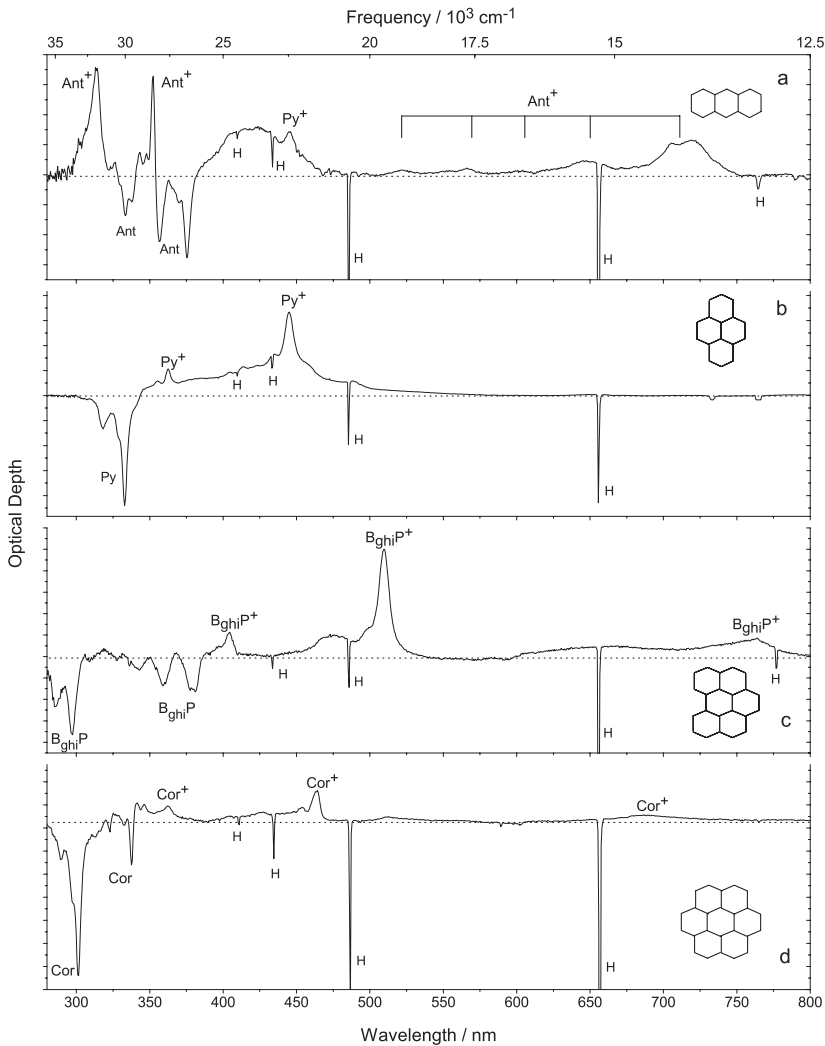
Figure 1. Four solid state surveys of different PAHs and their corresponding PAH cations embedded in amorphous solid water. The negative signals indicate use-up of a precursor species upon Ly-α irradiation, the positive signals represent the formation of new species, largely positively charged PAH species. Taken from Bouwman *et al.* (2009).

The use of the idea presented here applies also to other species. With OASIS it has been possible to measure, for example, the vibronic spectra of C_{60} in ice (Cuylle *et al.* 2012b), and in a similar way also other species may be studied. The general concept is to freeze potential DIB carriers, to record their optical ice spectra in a water ice matrix for astronomically relevant temperatures and to search for coincidences in the dense and not in the diffuse interstellar medium.

It is exactly here that astronomical data are strongly needed, as optical ice spectra basically do not exist. This is not surprising, as the number of suitable targets are very limited. Observations towards stellar objects are needed with well known stellar lines in the region of interest, that are known to be surrounded by ice, and with a visible extinction low enough to allow also for UV photoprocessing, to simulate (at least to some extent) processes as taking place in the diffuse ISM.

The idea presented here is new, and based on a number of assumptions. As stated before DIB carriers are assumed to survive the transition from diffuse to dense cloud conditions or alternatively to be formed in the dense ISM in a similar effective way as in the diffuse ISM. In the case that transient species are involved, the lower radiation fields in the dense ISM will affect their abundances. It is assumed that Ly-α induced reactions in ices simulate at least partially the solid state equivalents of transients in the diffuse medium. These processes in the solid state may be completely different, but clearly for PAH and PAH-cations this works well. Alternatively, if stable species are involved, it is likely that their radiation induced destruction rate in dark clouds will be less, and this may be even an advantage. It is far from sure that DIB carriers are present or formed under dense interstellar cloud conditions, but the opposite cannot be stated either. Therefore, it would be useful to aim for an optical solid state ice spectrum, to be compared with the available DIB data. A strong and isolated DIB, such as the λ 4430 feature, for example, may show up, and this definitely will provide a new view on potential carriers.

Acknowledgements

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