3.1 Bericht Teilprojekt 9

3.1.1 Titel / Title

Infrarot-Spektroskopie und -Lichtstreuung von Teilchenagglomeraten

Infrared spectroscopy and light scattering of dust agglomerates

3.1.2 Berichtszeitraum / reported period

01.07.2003 - 30.06.2006

3.1.3 Projektleiter / priniciple investigator

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3.1 Zusammenfassung / Abstract

3.2.1 Wortlaut des Antrags / abstract of the proposal

Dieses Projekt setzt einerseits die Arbeiten in TP 9 fort, indem die Infrarot-Extinktion durch Teilchen und Teilchen-Agglomerate in den Schwingungsbanden des Materials gemessen werden soll. Dabei soll der in der vergangenen Projektphase entwickelte experimentelle Aufbau benutzt werden. Andererseits sollen in diesem Projekt mit der Messung der Streukoeffizienten der Teilchen Aspekte von TP 10 weiter verfolgt werden, dies soll jedoch jetzt ebenfalls im infraroten Spektralbereich geschehen. Beide Messungen sollen an den gleichen Ensembles frei fliegender Teilchen in einer Niederdruck-Gasumgebung geschehen. Die Kombination von Streu- und Extinktionsmessungen soll eine umfassende Untersuchung von Form- und Agglomerationseffekten auf die optischen Eigenschaften der Teilchen ermöglichen.

This project is aimed to continue TP 9 in measuring infrared extinction by particles and particle agglomerates in vibrational bands with the experimental setup developed in the preceding project phase. In addition, we intend to continue part of the work previously done in TP 10 by measuring the particles' scattering coefficients, but now in the infrared spectral range. Both types of measurements will be done on the same ensembles of free-flying particles in a low-pressure gas environment. The combination of these measurements will allow us to study in a comprehensive way the effect of particle shape and agglomeration on the optical properties of solid particles.

3.2.2 Zusammenfassung des Berichts / abstract of the report

In this project, we have measured for the first time the infrared absorption spectra of *free-flying* silicate and oxide particles, i.e. of particles dispersed as an *aerosol*. We have obtained spectra in the wavelength range from 5 to 30 µm for amorphous and crystalline silicates of different compositions as well as for aluminum/magnesium and titanium oxides. Unlike previous approaches, this experiment allows a direct comparison of laboratory-measured infrared data of small particles with astronomical spectra of "dusty" environments such as AGB star atmospheres, accretion disks and planetary systems. Such comparisons have been carried out for a few objects so far and the differences to data obtained with classical spectroscopic methods have been quantified (Tamanai et al. 2006a).

Second, using this method we were able to investigate correlations between the spectral band profiles and the shape and agglomerate structure of the particles as seen by electron microscopic imaging. In this course we have investigated the spectra of powders with different grain shapes and identical composition and we have studied the influence of agglomeration on the spectra of spherical SiO_2 particles. Using theoretical light-scattering models, we have simulated the effects of agglomeration and of grain shape distributions and have compared the results with our measured band profiles (Tamanai et al. 2006b). This allows to interprete the measured spectra and to calibrate the geometrical parameters of the light-scattering models (Mutschke et al. 2006 and paper in preparation).

The infrared *scattering* measurements proposed in the project proposal could not be carried out because of (1) an accident during the setting up of the absorption spectroscopy experiment which damaged the setup and delayed the experimental activities, (2) the wide range of applications which the successful absorption spectroscopy experiment opened after it was working and (3) the necessary extensive theoretical simulation work, including a check of the applicability of light-scattering models in strong infrared bands (Andersen et al. 2006), which was carried out before the experimental work started.

3.3 Ausgangsfragen, neuster Stand der Forschung / Initial goals, current status of the field

Absorption spectra of solid particles small compared to the wavelength show pronounced bands due to the excitation of lattice vibrations. These bands are characteristic for the compound and its crystal structure and are of high analytical value. Apart from the dependence on the material, however, they depend also on the grain size, shape and the environment of the particle (e.g. Fabian et al. 2001). Classical infrared spectroscopic methods such as the measurement of absorption spectra from powders embedded in a KBr or polyethylene pellet result in changes of the band profile compared to the spectral characteristics of free particles such as cosmic dust grains (Tamanai et al. 2006a). On the other hand, the calculation of absorption band profiles is difficult for realistic grain shapes because exact methods such as the discrete dipole approximation tend to have large errors in regions of strong absorption (Andersen et al. 2006). Statistical methods using a parametrization of the average geometrical properties of an ensemble of particles require calibrating the free parameters for the particle geometry (Min et al. 2006). Measured spectroscopic data in the presence of information about the grain geometry, however, are rare, especially if the state of the particle agglomeration is considered.

On the other hand, there is a growing number of observations in the infrared wavelength region which aim at the investigation of dust properties in the interstellar medium including other galaxies, evolved stars, and especially young stars with accretion disks and planetary systems. Observations from the ground (e.g. Honda et al. 2003, Przygodda et al. 2003, van Boekel et al. 2004, 2005, Schütz et al. 2005a,b) and from space using the Infrared Space Observatory (e.g. Meeus et al. 2001) and nowadays the Spitzer Space Observatory (e.g. Kessler-Silacci et al. 2006, Furlan et al. 2006) have investigated emission band profiles of dusty circumstellar disks and outflows and have begun to extract from these band profiles information about dust mineralogy and grain size. The reason is that the dust properties trace physical conditions such as thermal structure, density and transport mechanisms in these environments (Bouwman et al. 2001).

Consequently, there is an expanding need for understanding the details of the infrared spectra of silicate and oxide particles. With this project we have provided an important contribution to the current progress in this field.

3.4 Angewandte Methoden / Experimental methods

3.4.1 Aerosol generation and spectroscopy

In this project we have built up a system for aerosol generation and spectroscopy, consisting of (1) a spectroscopy chamber connected to an FTIR spectrometer (Bruker 113v) and equipped with mirrors for multiple reflection of the infrared spectrometer beam and a pyroelectric detector and (2) an aerosol generator with a rotating-brush disperser (Palas RGB 1000) and a self-constructed impactor (see Fig.1).

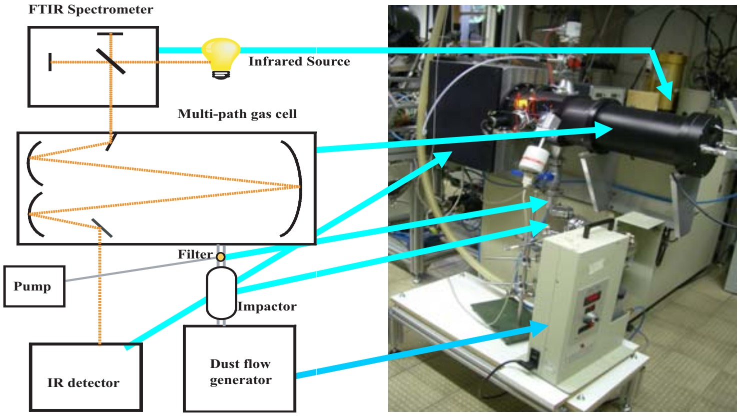

Fig. 1: Schematic setup and photo of the aerosol spectroscopy experiment.

During operation the rotating-brush disperser transports particles having grain sizes between 0.1 and 5 μm from a powder storage into a gas flow (N_2), which then carries the particles through the impactor to the gas cell. The impactor is able to retain larger clumps of particles and, on the other hand, densifies the aerosol by removing some of the carrier gas. A filter can be inserted into the gas flow in order to sample particles for scanning electron microscopy (SEM). Typical electron micrographs of the aerosol particles are shown in Fig.2. With this aerosol the spectroscopy chamber is partly filled, while additional continuous gas flows from the side protect the mirrors from contamination with particles. The aerosol density in the chamber is 10^5-10^6 cm^{-3} allowing for high signal-to-noise spectroscopic measurements in absorption bands with 32 passes of the infrared beam through the aerosol chamber.

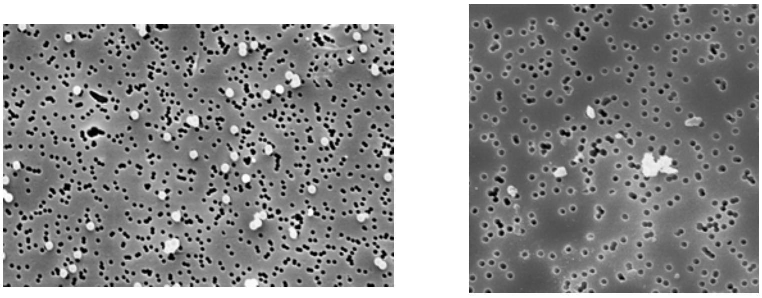

Fig. 2: SEM images of spherical SiO2 particles of 1 μm diameter (left) and Mg2SiO4 (forsterite) particles (right) sampled from the aerosol. The filter pores (dark spots) are 0.4 μm in size

3.4.2 Pellet spectroscopy

For comparison and for additional information we have applied the conventional pellet technique, where a small amount of sample material is mixed with IR transparent KBr or polyethylene powder at a mass ratio of e.g. 1:1000 and is pressed to a pellet of 0.2 g mass. The pellet is placed in the spectrometer beam for extinction measurements. The measurements with this widely used method are important to investigate differences in the measured band profiles between free-flying and embedded grains (see Sect. 3.5.1). Moreover, they provide quantitative information in terms of the mass extinction coefficient which can be used for calibration of the aerosol measurements and they give an independently measured result which can be compared to calculations (Sect. 3.5.3).

3.4.3 Computation of extinction spectra

For the spherical SiO_2 particles we have used exact light scattering theory in order to investigate the effect of particle agglomeration on the extinction spectra. In this course, a T-matrix code (Mackowski 1994) and the Discrete Dipole Approach (DDSCAT, Draine 1988) have been applied. Although we have shown that these methods may fail to converge in strong absorption bands (Andersen et al. 2006), for the optical constants of SiO_2 they give sufficiently accurate results (see Sect.3.5.2).

In case of all other samples, we have compared with calculations of extinction spectra based on a statistical approach. This model takes a con-tinuous distribution of particle shapes (shape factor distribution - SFD) into account (Min et al. 2006). We have determined the SFDs from the measured band profiles for a number of our samples (see Sect. 3.5.3).

3.5 Ergebnisse und ihre Bedeutung / Results and their importance

3.5.1 Comparison of aerosol and pellet spectra

Up to now, 15 different silicate and oxide materials have been measured using both the aerosol and pellet techniques. Among them are the crystalline silicate minerals forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$) and their amorphous counterparts as well as amorphous and crystalline SiO_2. These compounds are the most abundant solids in space.

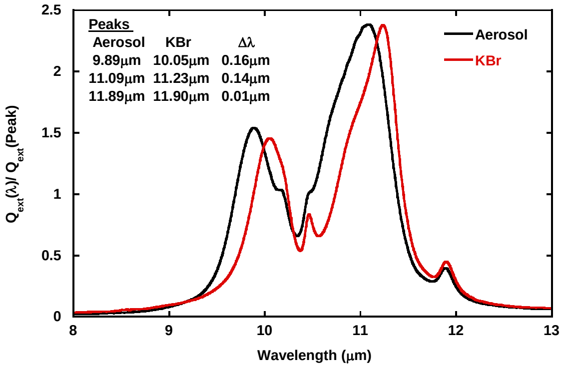

Fig. 3: Normalized extinction cross section for forsterite particles (commercial material from Alpha Johnson) measured for free (aerosol) and embedded (KBr) particles.

Their spectral signatures are observed in most dusty environments in space and are analyzed for variations in the chemical composition, crystallinity, and size of the dust grains. Accurate information on the shape of the band profiles is therefore extremely important, especially for the spectral range of the Si-O stretching vibrations (8-13 µm) which can be observed from ground and are therefore most widely investigated.

Fig.3 shows our results obtained in this spectral range with the aerosol and the pellet methods for a synthetic forsterite powder. The Figure demonstrates the significant difference between the band profiles measured using these two different techniques. The positions of the strong peaks in the band are generally at shorter wavelengths for free particles. Small peaks do not shift but can change to shoulders by merging with the strong bands.

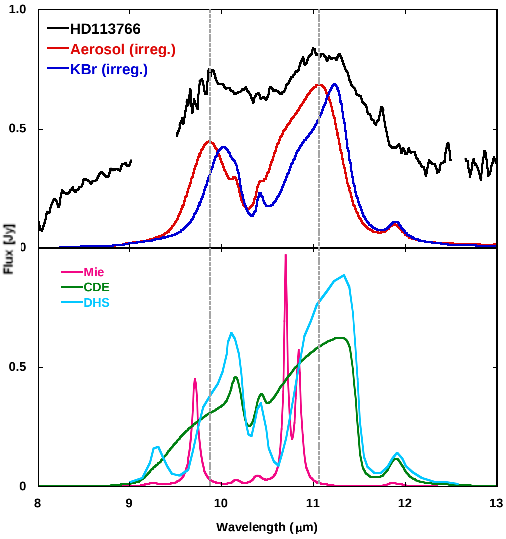

Fig. 4: Comparison of the measured spectra from Fig.3 with the observed spectrum of the main sequence object HD 113766 and with simulated forsterite spectra obtained using different light-scattering theories. The vertical lines indicate the positions of the main peaks in the aerosol spectrum.

Whereas the aerosol spectrum can directly be used for a comparison with an astronomical spectrum, the pellet result would give wrong results. This is demonstrated in Fig.4 by comparing with the observed spectrum of a main sequence star with dusty disk and with several simulated spectra. The spectrum of the free forsterite particles coincides with a peak at 11.1 µm in the observed spectrum but not with the maximum at 11.3 µm, which would match to the spectrum of the embedded grains. Furthermore, the calculated spectra using the Mie theory, the classical Continuous Distribution of Ellipsoidal shapes (CDE, Bohren and Huffman 1983), or the more advanced Distribution of Hollow Spheres (DHS, Min et al. 2005) do not reproduce the measured band profiles (Tamanai et al. 2006a). This underlines the importance of our results and of a mandatory improvement of the theoretical approaches.

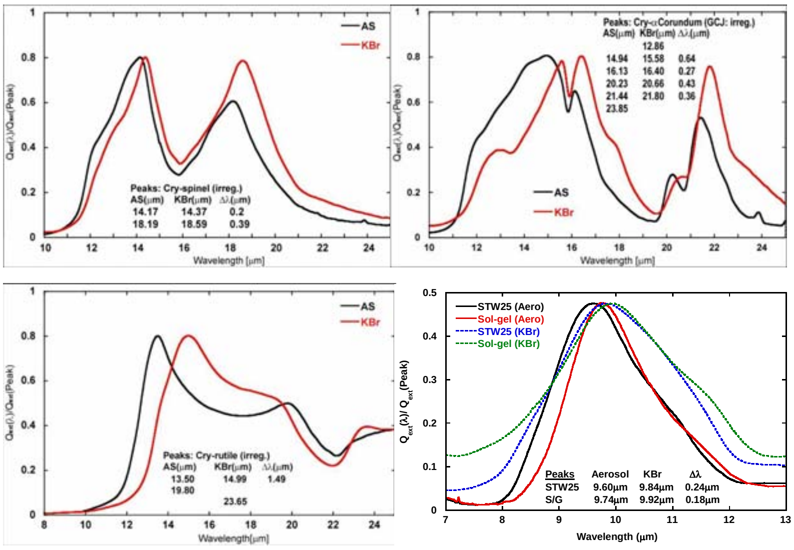

Fig. 5: Comparison of aerosol (AS) and pellet (KBr) spectra for various oxides (corundum – Al_2O_3, spinel – $MgAl_2O_4$, rutile – TiO_2) and two amorphous silicates of approximate composition $MgSiO_3$ (STW25 is a melting/ quenching, S/G is a sol-gel process product – Dorschner et al. 1995, Jäger et al. 2003).

Even more pronounced is the influence of the embedding medium on band profiles for some oxide materials such as Al_2O_3, TiO_2, and $MgAl_2O_4$ (see Fig.5, upper and left panels). These compounds are high-temperature condensates in oxygen-rich environments and are considered to dominate the emission from some lower-mass-loss AGB stars (Posch et al. 1999, 2003). The difference in the position of absorption peaks between embedded and free-flying particles can amount to about 1.5 µm in these cases.

Even for amorphous silicates which represent the most abundant dust material in space the effect of an embedding medium is not negligible (Fig.5, lower right panel). Although this effect is in principle known and can be approximately calculated for simple grain geometries, this is the first time that it had been quantified by measurements for a number of important and real dust materials.

3.5.2 Effect of agglomeration

In contrast to the pellet method, the aerosol technique bears the capability of studying the influence of grain growth by agglomeration on spectroscopic features experimentally. In a first approach, we have investigated the effect of larger aggregates on the spectrum by varying the abundance of clumps left from imperfect de-agglomeration in the disperser. By removing the impactor from the aerosol line, we allowed larger clumps to reach the spectroscopy chamber. There, the biggest and more compact ones settle down quickly, but smaller and more open aggregates are easily carried by the gas in addition to the well-dispersed particle fraction. Fig.6 shows an SEM image of such larger clumps together with the IR band profiles measured for SiO_2 aerosols which have been produced with and without use of the impactor (compare Fig. 2).

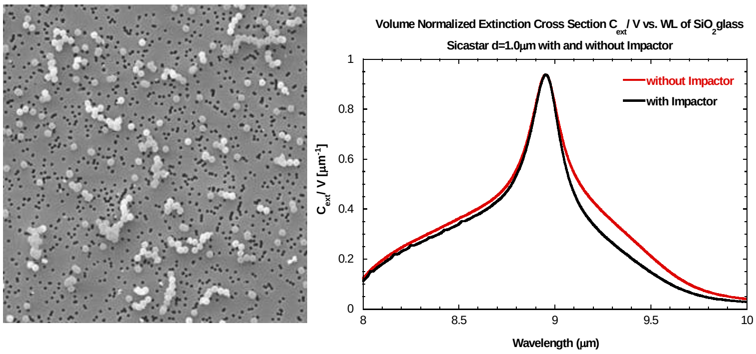

Fig. 6: SEM image and band profile obtained for SiO_2 particles without use of the impactor .

The effect of the aggregates is obviously the strengthening of a wing at the long-wavelength side of the band profile. This is supported by calculations using exact light scattering theory for aggregates of spherical SiO_2 particles (see Fig. 7). Apart from a slight mismatch of the peak position, which may be caused by a deviation in the particle's optical constants from the bulk SiO_2 properties, these calculations demonstrate that aggregation leads preferentially to an increase of the extinction in the long-wavelength wing of the band (Tamanai et al. 2006b).

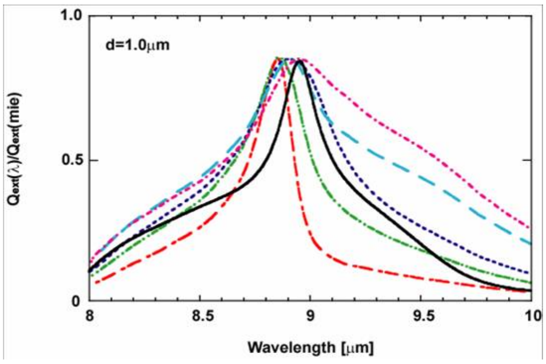

Fig. 7: Comparison of the measured band profile of SiO_2 particles (d=1.0 µm, black) with calculations for various cluster geometries using the DDSCAT code. The simulated spectra are for a single sphere (red), two touching spheres (green), a tetrahedral aggregate of four spheres (blue) and two irregular clusters of 16 spheres (light blue and magenta).

In a theoretical study, which has been performed in collaboration with colleagues in Copenhagen, Vienna, and Amsterdam, we have investigated the applicability of the DDA and T-matrix approaches for calculation of infrared band profiles for agglomerate particles composed of other materials (Andersen et al. 2006). We have demonstrated that, for resonances in which the real part of the refractive index becomes close to zero (as is the case, e.g. in the IR band of SiC) neither of these exact light-scattering calculations reaches a convergence even with very high dipole densities in the DDA or very high multipole numbers in the T-matrix calculations. Fortunately, for SiO_2 the resonance strength is moderate enough to allow at least approximate results which are shown above.

3.5.3 Shape effects and shape factor distribution

For nonspherical particles, even if they can be considered to be small compared to the wavelength, statistical light-scattering approaches are needed to reproduce or predict band profiles. However, as has been demonstrated in Fig.4, models assuming simple distributions of shape factors such as the CDE or DHS do not reproduce measured band profiles in all detail. For a better fit, they need to be calibrated, i.e. shape factor distributions for certain particle shapes need to be determined.

The spectra measured in aerosol and in KBr provide valuable information for this purpose. Moreover, for some of the materials studied in this project, we were able to investigate particles with different shapes. Fig.8 shows spectra of forsterite powders obtained from two different sources (Marusu and Alpha Johnson, respectively) of which the former particles have a roundish shape whereas the latter have a sharp-edged, irregular shape (see the

TEM images in Fig.8). Likewise, in Fig.9 we show the spectra of two Al_2O_3 powders with different particle shapes.

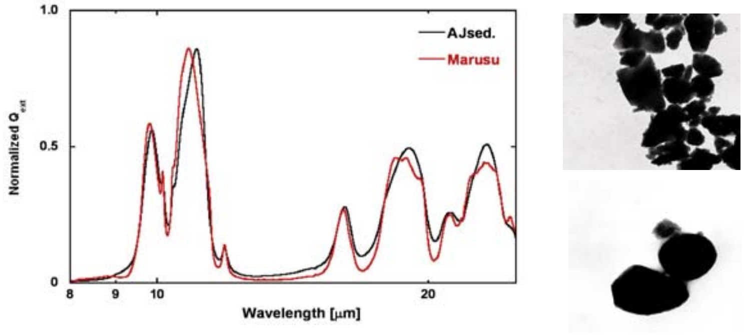

Fig. 8: Influence of particle shape on the forsterite (Mg_2SiO_4) band profiles. Grains of sample AJsed (Alpha Johnson after sedimentation, upper TEM image) have a sharp-edged shape whereas grains of sample Marusu (lower image) are round.

For both minerals, the measured spectra demonstrate a strong influence of the particle shape on the measured band profiles. Generally, for roundish (or ellipsoidal) grains the peaks of the bands are located at shorter wavelengths compared to those of the irregular grains. This is not only true for the aerosol-measured spectra but also for the pellet spectra (see Fig.10, right panel).

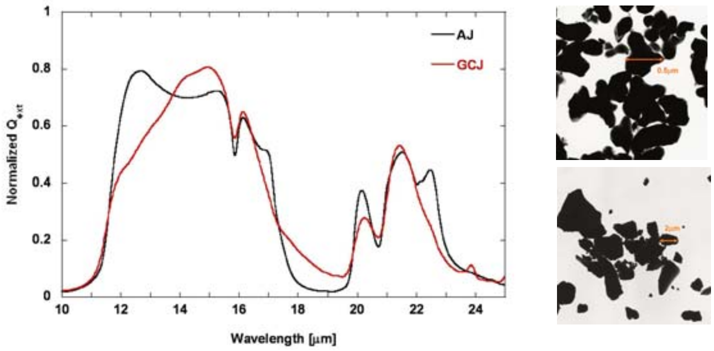

Fig. 9: Influence of particle shape on the corundum (Al_2O_3) band profiles. Sample AJ (Alpha Johnson, upper TEM image) has a roundish grain shape whereas grains of sample GCJ (Institute for Glass Chemistry Jena, lower image) are sharp-edged.

For one of the materials (forsterite), we have demonstrated that the measured spectra can be reproduced using suitable shape factor distributions (SFDs, Mutschke et al. 2006). These SFDs depend on the characteristics of the grain shape but are of course independent on the em-bedding medium used in the measurement. Consequently, they reproduce both the aerosol and pellet spectra at the same time (Fig.10). This is the first time that light-scattering models have been calibrated according to the influence of the grain shape for real ensembles of particles.

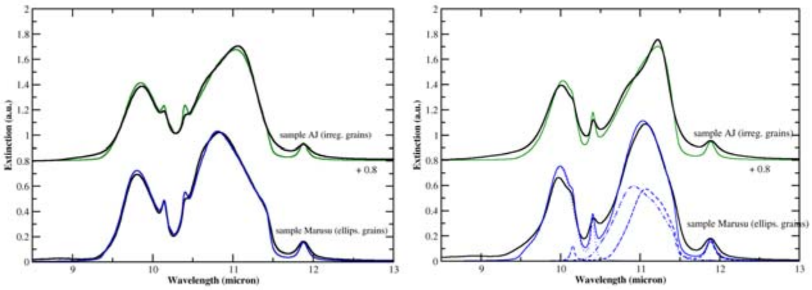

Fig. 10: Comparison of measured (black lines) and calculated spectra using special shape factor distributions for the two different forsterite powders. Left panel is for measurements in aerosol (same as in Fig.8), right is for embedded particles. Identical shape factor distributions are used for left and right. The dotted lines indicate the contributions from fields along the three forsterite crystal axes.

3.6 Zusammenfassung und Ausblick / Summary and future

The project carried out during the reported period has led to the development of a very promising experiment which in contrast to previous approaches allows (1) direct comparison of experimental and astronomical infrared spectra of solid particles, (2) the investigation of band profiles in dependence on shape and agglomeration of the particles and (3) the calibration of statistical light-scattering models for these influences.

We have recently applied for support by the DFG for a new research project which would make use of this experiment for further measurements, aiming at the development of a database of dust aerosol spectra for application to the modeling of debris disks and a continuation of the work on the calibration of light scattering models.

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