

Application for Extension of Financial Support of

**Project 5:  
Studying Zeolitic Diffusion by  
Interference and IR Microscopy**

as part of a package of proposals  
aspiring joint support by CNRS, DFG, EPSRC and NSF

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# 1. General Information

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## 1.2. Topic

Studying Zeolitic Diffusion by  
Interference and IR Microscopy

## 1.3. Code Word

Diffusion by Microscopy

## 1.4. Research Areas

Material Sciences  
Chemical Engineering  
Physical Chemistry  
Interface Sciences

## 1.5. Scheduled Total Duration of Support

six years, support by DFG since 2003

## 1.6. Period of Support Applied for

three years

## 1.7. Total Period of Support

support started November 2003,  
extension requested starting from November 2006

## 1.8. Summary

Interference microscopy and IR microscopy are so far the only two techniques, which allow the direct observation of the evolution of concentration profiles in the interior of zeolite crystals. Purposefully exploiting this option during the first period, a number of crucial parameters of molecular transport in nanoporous materials have been shown to become accessible in an unprecedented way by direct experimental observation. They include the first microscopic application of Fick's second law to the evolution of intracrystalline concentration profiles, the direct measurement of surface barriers and, vice versa, of sticking coefficients and the direct measurement of anisotropic intracrystalline transport diffusion. Moreover, with the advent of the IR microimaging system, funded via the separate DFG project KA 953/20-1,

in presumably January 2007 also a discrimination between different molecular species with spatial resolution down to a couple of micrometers shall be possible, so that now also multi-component diffusion becomes accessible to these novel options of measurement. It was the original intention of the package of application, to contribute by the microscopic techniques to as many problems as possible raised by the "conventional" techniques. In addition to this task, however, the innovations in the experimental techniques attained by the introduction of these new measuring principles, also suggest the reverse procedure, viz. to explore up to which extent the qualitatively new evidence provided by these microscopic techniques may be corroborated by the other measuring techniques of the consortium, possibly also including the choose of further nanoporous host systems. Both of our microscopic techniques of diffusion measurement are so far confined to room temperature. Comparison with other techniques, as well as the evidence provided by the measurements, would highly benefit from the option of temperature variation. Commencing with interference microscopy, the prerequisites for temperature-dependent measurements shall also be cared for within the project.

## **2. State of the Art, Own Activities in the Field**

### **2.1. State of the Art**

As an ingenious alternative to the gravimetric method, H. Karge for the first time applied IR spectroscopy for the observation of sorption phenomena on zeolites [1-6]. This approach offers the important advantage that, by a judicious choice of the IR wavelength, the sorption of any individual component may be followed separately. Consequently, among the numerous investigations of the last few years dedicated to diffusion in nanoporous media in general, including such topics like molecular modelling [7-15], technical utilization [16-21], novel measuring techniques [22-25], diffusion anomalies [26-33] and the measurement of "new" systems [34-45], one may find an increasing number of studies by IR spectroscopy [6, 46-52]. However, the potentials of IR monitoring are by far not exploited by these studies. Non of these studies includes spatially and temporally resolved measurements of transient sorption. In fact, so far only in our own studies reported in [53, 54] first attempts of this type of measurement, as an indispensable prerequisite for the direct observation of intracrystalline diffusion by this technique, have been made.

With the advent of IR focal plane array detectors [55-58] in the last few years, however, the spatial and temporal resolution attainable by IR imaging has notably enhanced, reaching the range of a few micrometers and seconds. Starting from January 2007, with the IR imaging device Hyperion 3000 of the BRUKER company, funded by the DFG via the project KA 953/20-1, we shall dispose of this option.

An even better spatial and temporal resolution may be attained by interference microscopy. For the investigation of single-component sorption phenomena, where there is no need for spectral discrimination between different species, interference microscopy is therefore notably superior to IR imaging. To the best of our knowledge, there are presently no other groups exploiting this technique for diffusion studies with nanoporous materials. This might be related to the fact that with our - DFG supported - application ten years ago we acquired one of the last interference microscopes of type Jenamap which, following the Mach-Zehnder principle, offers particularly favourable conditions for the observation of dynamic processes by interference microscopy.

## 2.2. Own Activities in the First Period

Following first, preliminary studies demonstrating the novel options of interference microscopy with snapshots of methanol adsorption by zeolite NaCaA [59, 60], with the quantitation of internal transport barriers in MFI-type zeolites [61-63] and with revealing dramatic deviations from the ideal textbook structure for zeolites of type AFI [53, 64-67], in particular interference microscopy was shown to open up completely new routes to the experimental determination of crucial parameters of mass transfer. This concerns the microscopic application of Fick's second law to determine the complete concentration dependence of zeolitic transport diffusivities during uptake and release experiments, the simultaneous determination of all principal elements of the diffusion tensor by analysing the spatial-temporal development of concentration profiles during adsorption on anisotropic zeolite crystallites and the quantitation of surface resistances and, vice versa, of the sticking probability on zeolite crystallites [54, 68]. As a further application, for MOF manganese formate as a model system for 1d structures, molecular diffusion could be shown to ideally proceed in one dimension. Four publications are in preparation: "Direct measurement of orientation-dependent diffusion in nanoporous crystallites" by P. Kortunov, M. J. Castro, D. Tzoulaki, J. Kärger, P. A. Wright, "Surface barriers and their influence on transient sorption by A-type zeolites" by D. Tzoulaki, P. Kortunov, M. Krutyeva, S. Vasenkov, J. Kärger, X. Yang, J. Caro, "Measurement and analysis of internal concentration profiles in nanoporous materials" by J. Kärger, P. Kortunov, S. Vasenkov, L. Heinke, C. Chmelik, D. Tzoulaki, D. B. Shah, R. A. Rakoczy, Y. Traa, J. Weitkamp, "Internal concentration gradients in nanomaterials: measurement and microscopic analysis" by L. Heinke, P. Kortunov, C. Chmelik, D. B. Shah, J. Kärger, (2006), see also [69, 70].

As the practically most important message of these studies, the various types of transport resistances inherent to zeolite crystallites are found to lead to patterns of the time dependence of uptake and release which, without this knowledge, are attributed to completely wrong limiting mechanisms [71]. Thus, interference microscopy in combination with IR microscopy may be suggested as a powerful tool to unveil "disguised kinetics".

Methodological development in the field of interference microscopy has notably contributed to the success of this project and was honoured by awards delivered to Pavel Kortunov for his merits on the German Zeolite Conference, Hannover, and on the first International INSIDE-PORE Workshop, Montpellier, both in March 2006. These developments include the new installed PC with enlarged graphic opportunity for interference microscopy and the additional "home-written" software which allows calculating the experimental results more precisely and with higher quality. Also a new design of the adsorption system has been elaborated which, last not least, includes extra-precautions for leak-tightness during the whole procedure of sample activation and adsorption-desorption runs. In particular in the case of hydrophilic zeolites, operating with a very small number of crystals turned out to include an incredibly high risk that already faintest amounts of water vapour entering the system will block the crystals under study by their preferential adsorption.

## 3. Issues and Working Programme

### 3.1. Issues

The potentials of interference and IR microscopy as elaborated and demonstrated during the first period with qualitatively new insights into molecular uptake and release on nanoporous particles shall be exploited in tense interaction with the other techniques. These joint

activities will concern the measurement of intracrystalline diffusion, surface permeability (including information about sticking coefficients) and internal transport barriers.

For interference microscopy the option of temperature variation shall be provided to ensure an extended range of measurement and the option of extrapolation beyond the directly accessible temperature range. This option is indispensable for guaranteeing a sufficiently large overlap of the measuring conditions with the other techniques. Moreover, knowledge of the temperature dependences of the transport-related parameters accessible by these experiments most significantly improves the options to deduce a meaningful picture of the micro-kinetic mechanisms from the observed transport phenomena.

In addition to the observation of single-component phenomena, starting from January 2007 with the option of IR micro-imaging also tracer-exchange, co-and counter-diffusion shall be observed.

### **3.2. Working Programme**

After development and completion of the device for interference microscopy for measurements at ambient temperature during the first period, the application of the technique shall be optimized with respect to a maximum output of possibilities to correlate the results with those of other techniques within the consortium. This concerns in particular the option of temperature variation. For this purpose, following measures are planned:

- (i) The main parts of the adsorption system including the large gas reservoir, pressure gauges, valves, tubes and the optical cell are planned to be isolated from the surrounding atmosphere by using thermo-isolated materials (see fig. 1)
- (ii) The thermo-isolated system will contain the equipment for heating/cooling the air inside the system and several fans for temperature homogeneity over the system
- (iii) The details of the adsorption system (especially pressure gauges and vacuum components) have to be selected in such a way that their proper operations are also guaranteed in the high- and low-temperature range.
- (iv) We plan to use the flow of heated/cooled air around the optical cell to keep the temperature of the crystals under investigation identical with the temperature of the adsorption system.
- (v) The connections between the inside part of the adsorption system and outside parts (vacuum pump, ampoule with liquid, balloon with gas) are planned to be as small as possible in order to minimize the heat transfer from outside to inside and vice versa
- (vi) Several pressure detectors are planned to be included into the different parts of the system (large gas reservoir, optical cell, pressure gauges and so on) in order to check the identity of the temperatures over the system.

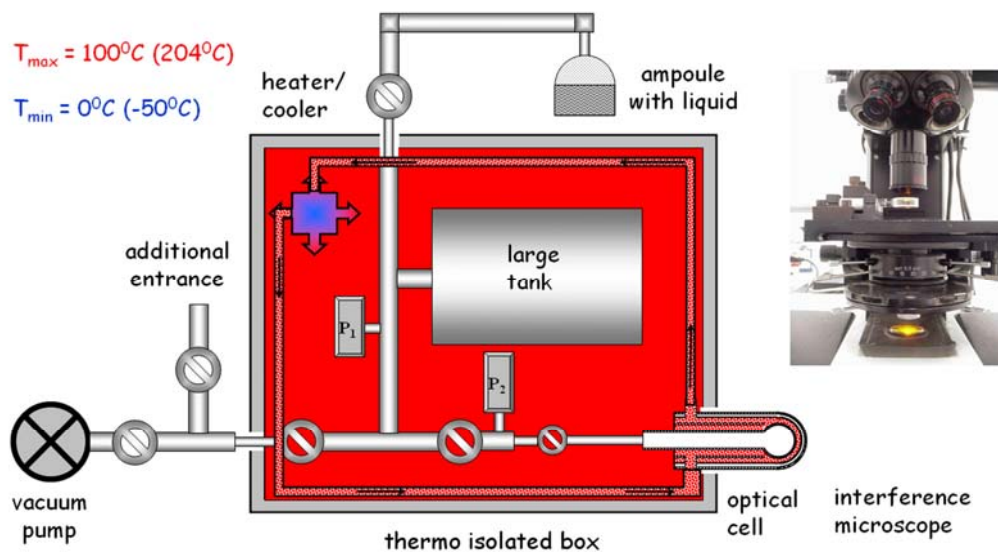


Fig. 1: Schematic representation of the planned activities for ensuring diffusion measurements by interference microscopy over an extended temperature range.

Taking into account the temperature ranges allowing a proper operation the individual components, as a first step, adsorption/desorption experiments at temperatures from  $0^{\circ}\text{C}$  up to  $100^{\circ}\text{C}$  should become possible, with the further option to enlarge the range from  $-50^{\circ}\text{C}$  up to  $204^{\circ}\text{C}$ . The option of temperature variation opens a new dimension for investigating zeolitic diffusion by interference microscopy, including the option to vary the relative influence of surface resistances and intracrystalline diffusion on the overall uptake, release and exchange rates and the determination of the respective energies of activation. This type of information, inaccessible so far, is crucial for an unequivocal attribution of the observed transport phenomena to their microstructural and microdynamic origin.

For the performance of IR microscopy, starting from January 2007 the BRUKER IR imaging system Hyperion, 3000 acquired within the frame of the DFG project KA 953/20-1,2, is under our disposal. After exploration of its potential as a high-tech device with optimized space- and time resolution at ambient temperature, including the observation of multi-component phenomena like tracer exchange and counter- and co-diffusion, following the example of interference microscopy, also the possibility of temperature variation will be cared for.

### 3.2.1. LTA

As one of the most intriguing results obtained during the first period of support, for n-alkanes in zeolite NaCaA notable deviations from a monotonic dependence of the diffusivities on the chain length has been observed [72, 73], in particular in the range from 7 to 12 carbon atoms. Our attempts by interference and IR microscopy to contribute to this issue led to the important result that single-crystal experiments with such highly hydrophilic host systems like zeolite NaCaA require particular precautions against faintest leakages which proved to be irrelevant for the other systems. First successful adsorption and desorption measurements with ethane and propane on zeolite NaCaA are just being performed, so that now all options are given to directly follow the evolution of intracrystalline concentration profiles as a function of the chain length and - as soon as the technical prerequisites are given - of the temperature.

Most importantly, in this way a direct discrimination between the intracrystalline transport resistances and those on the outer surface (including the finite rate of guest supply out of the gas phase) may be provided and the effect of a deliberate variation of the intensity of surface resistances (e.g. by TEOS treatment - see project 1) and its variation with chain length and temperature may be recorded.

Thus, important additional experimental evidence is provided which has to be incorporated in search of the origin for the different patterns provided by the so far applied techniques (QENS, PFG NMR and ZLC) for the deviations from a monotonic decrease of the apparent diffusivities with increasing chain lengths.

Further, diffusion studies shall be performed with sub-critical methanol vapor. Methanol in NaCaA was the first system, in which intracrystalline transport diffusion could directly be observed via interference microscopy [59, 60]. Moreover, due to the presence of the bivalent calcium ions in the zeolite bulk phase, the intracrystalline diffusivity of methanol as a polar molecule may be expected to be additionally slowed down, which might provide the option of reducing the relative influence of surface barriers. Since in our last studies the presence of faintest traces of water has been found to dramatically corrupt (to even exclude!) the measurements with normal alkanes, the option of data corruption has to be taken into account also in the case of methanol - urgently requiring the reproduction of these old measurements.

In cation-free LTA a dramatic enhancement of the intracrystalline diffusivity should be observed. This should in particular concern the polar methanol molecules, so that their diffusivities should get closer to those of methane and ethane, as has been found already by preliminary PFG NMR studies [74]. In turn, owing to the enhanced intracrystalline diffusivities, better options for a detailed study of possible surface barriers are provided. Whether the relevant measurements by interference and IR microscopy may in fact be performed depends on the crystal size of the cation-free LTA emerging from the efforts in zeolite synthesis.

Zeolite NaCaA represents an ideal model system for multicomponent diffusion studies via IR micro-imaging. The measurements shall in particular include mixtures of small chain length (ethane, propane) and large chain length (n-hexane) n-alkanes. Following both the general predictions of irreversible thermodynamics [75] and the application of the Maxwell-Stefan formalism to zeolites [76, 77] in this case correlation between the single- and two-component diffusivities can be expected to be mainly mediated by the thermodynamic factor rather than by micro-kinetic correlations. The particular relevance of such studies within the research group results from the fact, that only by this technique an unambiguous, since direct, discrimination between surface- and bulk-resistance effects is possible.

### **3.2.2. *Silicalite-1/ZSM-5***

In contrast to zeolite NaCaA where cubic symmetry allows the determination of microscopic diffusivities from the integral concentrations observed in the experiments [59, 60], diffusion anisotropy in MFI-type zeolites prohibits this direct access. Even more importantly, the MFI-"crystals" prove to be compound crystals so that, in general, the direction of observation by IR or interference microscopy cannot be attributed to one crystallographic direction. Moreover, the interfaces between the different compartments may give rise of additional transport resistances. An important step ahead to overcome these limitations may have been made within the consortium by the Mülheim group (W. Schmidt) with the separation of the compound crystals into their individual compartments, which are expected to represent genuine single crystals. Application of IR and interference microscopy to these

compartments, however, is complicated by the fact that their wedge-shaped form prohibits observation through two parallel crystal faces, which for the sake of a more direct data analysis is generally ensured in our experiments. Notable deviations from this case require further computational efforts and soft-ware development for data analysis.

Since, though being composed of individual compartments, the compound crystals of type MFI are generally available in well shaped (brick- or coffin-like) form they provide ideal conditions for applying interference and IR-microscopy. Hence, if one confines oneself to describing intracrystalline diffusion by one "effective" diffusivity, resulting from an appropriate average over the different direction-dependent values, the combined application of interference and IR microscopy may turn out to be a very productive technique for this type of zeolites. With the exception of a few PFG NMR experiments [78, 79] and uptake studies with oriented crystals [80], the usual way of analyzing diffusion experiments with MFI is in fact based on effective diffusivities [81-85]

In this way, IR and interference microscopy shall be applied to complement and support the evidence of monotonically decaying n-alkane diffusivities with increasing chain lengths, provided so far by QENS, PFG NMR and ZLC [86, 87] since, similarly as with zeolite NaCaA, studies by molecular modelling predict oscillating diffusivities with (further) increasing chain lengths [7, 10, 19, 88].

Most importantly, the ZLC experiments with n-alkanes in MFI-type zeolites of the first period revealed an even much more pronounced reduction of the diffusivities in comparison with the microscopic techniques than observed with NaCaA. Since ZLC partial loading experiments point to internal mass resistances rather than to surface barriers as the origin of these differences, a confirmation of this supposition by direct monitoring of molecular ad- and desorption is highly wanted.

On the other hand, in experiments with deliberately created surface resistances, following our preliminary investigations [54], in coordinated ZLC, gravimetric, (IR- and interference-) microscopic, PFG NMR and FR studies it has to be demonstrated that in this case also quantitatively coinciding information about the intensity of these surface resistances is provided.

In comparison with the n-alkanes, diffusion of branched n-alkanes and aromatics is notably reduced. While in the case of isobutane still essentially all techniques of diffusion measurement are applicable (including PFG NMR with the option of MAS), the diffusion of longer iso-alkanes and the aromatics shall most likely be accessible by only the macroscopic techniques and IR- and interference microscopy. Both the practical impact of such studies and the option to directly trace the influence of compatibility ("commensurability") of channel architecture and molecular shape on diffusion [89-93] make such studies highly desirable.

Multicomponent diffusion studies with mixtures of small chain length (ethane, propane) and large chain length (n-hexane) n-alkanes should reveal correlations between single-component and multicomponent diffusion on the one hand, and between transport and self-diffusion on the other, which include the influence of both (equilibrium) thermodynamics and molecular kinetics. Following either irreversible thermodynamics [75] or its extension by the Maxwell-Stefan formalism [76, 77], the influence of microkinetics, in addition to the omnipresent influence of the "thermodynamic factor", on the correlation between the different diffusivities may be rationalized as a consequence of the mutual hindrance of the molecules during propagation in the intersecting channels of the pore system. As a unique option in comparison with all other measuring techniques, IR micro-imaging permits the observation of the evolution of the intracrystalline concentration distributions of all components involved, in



particular under the conditions of co- and counter-diffusion and with tracer exchange.

### 3.2.3. *NaX*

The options to apply interference and IR microscopy to monitoring intracrystalline concentration profiles is confined to a rather limited space, viz. the space traversing the crystals between two opposite, parallel triangular crystal faces. Though measurements of this type are in principle possible, the conditions under which they have to be performed are therefore notably poorer than for all other host materials considered. Hence, most likely, IR- and interference measurements with NaX will be restricted to benzene/toluene and methanol as guest molecules, since they represent the limiting cases for compatible (methanol) and incompatible (benzene/toluene) results when comparing previous comparative experiments using different techniques of diffusion measurement [94-96].

### 3.2.4. *Ferrierite*

As a particular structural feature, the so far synthesized specimens dispose of 8-membered ring channels which are accessible on both crystal sides, while the entrance to the larger (10-membered ring) channels are on both sides blocked. The application of interference microscopy to zeolite crystals of type ferrierite offered the so far most spectacular results attained with this technique, including the measurement of genuine one-dimensional diffusion, of concentration-dependent diffusivities from the profile evolution and of surface barriers and the sticking probability correlated with them [71]. Hence, in combination with the other techniques, more detailed investigations to elaborate the interplay of intracrystalline diffusion and surface resistances is an attractive task for the future. Moreover, if the efforts of the synthesis groups to find routes to a deliberate variation of the accessibility to the two different types of channels shall be successful, ferrierite may as well turn out as an ideal model host for the investigation of single-file diffusion (via switching the accessibility from the small to the large channels) [66] and for molecular traffic control [97-99], where IR imaging will prove as an indispensable tool for discriminating between the different species and their diffusion paths.

### 3.2.5. *AlPO<sub>4</sub>-5*

So far, clear and unambiguous experimental evidence on the occurrence of pure one-dimensional zeolitic diffusion in general, and of single-file diffusion in particular, is missing [66]. While in transient experiments one-dimensional (including single-file) diffusion does not yield any peculiarities in comparison with multi-dimensional diffusion, the situation is completely different in self-diffusion and counter-diffusion experiments. In the latter case, molecular propagation is dramatically slowed down, resulting in the fact that molecular exchange with the surrounding scales with the third power of the file length (rather than with the second power as in the case of normal diffusion). The experimental demonstration of this peculiarity by both tracer-exchange and counter-diffusion experiments is in the centre of these studies. Moreover, monitoring the evolution of molecular concentrations over the 1D crystal structure will serve as a crucial test of the crystallographic perfection of the crystals, i.e. whether the efforts of the synthesis group to indeed synthesize crystals with a perfect 1D channel structure have been successful.

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## 4. Requested Financial Support

### 4.1. Personnel

The complexity of the task involving two different microscopic techniques and their instrumental development requires the employment of a post-doctoral fellow (Research

Associate, BAT IIa). For performing a part of the measurements, funding of a research student (studentische Hilfskraft) is applied for.

#### **4.2. Durable Equipments**

(including consumables, needed for temperature-variable interference microscopy)

Multi-layer organic glass materials for the thermo-isolated box	€1,500
Equipment for heating and cooling the air in the broad temperature range	€3,000
High-temperature pressure gauges	€4,700
High-temperature components for the adsorption system	€1,500
Thermo-sensors and display for temperature control	€500
Fans for air mixing and power supply	€500

#### **4.3. Consumables**

Pure and isotope-labelled substances	€5,000
Vacuum-tight glass cuvettes for IR microscopy	€2,500
Optically clean quartz glasses for the cuvettes for interference microscopy	€2,500

#### **4.4. Travelling**

Implying that the group meetings are ensured by central funding the travelling budget has primarily to be used for keeping personal contact with other laboratories, in particular in the field of zeolite synthesis and characterization (Prof. Terasaki, Stockholm) due to the new options and requirements provided by our microscopic techniques, and for conference participation (Annual German Zeolite Conferences, Conferences of the International Zeolite Association and Adsorption Association). Therefore, a total amount of 2000 €per year, corresponding to 6000 €for the total period of time, is requested for supporting visits and conference participation.

## **5. Requirements for the Success of the Application**

### **5.1. Team Members**

- a) Prof. Dr. Jörg Kärger (applicant)
- b) Dr. Pavel Kortunov (post doc of the International Research Training Group),
- c) Dipl.-Phys. Christian Chmelik (separate DFG project)
- d) Dipl.-Ing. Despina Tzoulaki (EC Marie Curie programme)
- e) Dipl.-Phys. Cordula Krause (research technician)
- f) Lutz Moschkowitz (technician)
- g) cand. phys. Lars Heinke (awardee Studienstiftung des Deutschen Volkes)

### **5.2. Cooperation with Other Scientists**

The primary partners of cooperation are the members of the consortium. Following a long cooperation, the investigations shall be carried out in close contact with Prof. Dr. D. M. Ruthven, Univ. of Maine, USA. (Humboldt Awardee 2002). Close contact shall be as well maintained with Prof. S. Vasenkov (University of Florida, Gainesville) who, as a member of our group before his appointment, notably contributed to the development of the microscopic techniques which are in the focus of this application.

With respect to IR microscopy, continuous contact with Dr. H. G. Karge, Berlin, shall be maintained.

### **5.3. Available Equipments**

Vacuum devices for out-of-system sample activation,  
Interference microscope Jenamap p dyn  
IR microscope FTS 6000/UMA 500, programmable sample holder  
(starting from January 2007) IR imaging system Hyperion 3000 (BRUKER)

### **5.4. Support from the Own Budget**

From the budget of the institute an amount of about 1000 € may be used for ensuring the operating conditions of the equipments.

### **5.5. Further Prerequisites**

The institute offers the working places for the co-workers, applied for, as well as the necessary laboratories. The infrastructure of the institute allows the use of data-networks and computer systems free of charge.

## **6. Statements**

### **6.1. Collaborative Research Centres (Sonderforschungsbereiche)**

The present application cannot be part of any of the existing collaborative research centres of the University.

### **6.2. Application for Support by Different Sources**

I have never applied for financial support of this or a similar project. If I shall do so, I will


immediately inform the German Science Foundation (DFG).

### **6.3. Information to the University Representative of DFG (Vertrauensmann)**

The university representative of the DFG, Prof. Dr. E. Hey-Hawkins has been informed about this proposal.

## **7. Signature**

Leipzig, June 19, 2006

A handwritten signature in black ink, appearing to read 'J. Kärger'. The signature is written in a cursive style with a prominent initial 'J' and a distinct 'K'.

Prof. Dr. Jörg Kärger