

Conformational order of *n*-alkyl modified silica gels as evaluated by Fourier transform infrared spectroscopy

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Abstract

The conformational behaviour of non-deuterated and selectively deuterated alkyl modified silica gels in the dry state is examined by variable temperature FT IR spectroscopy. In the present study, three systems are considered, which are distinguished by the length of the tethered alkyl chains (C_9H_{19} —, $C_{18}H_{37}$ —, $C_{22}H_{45}$ —). The desired information is obtained by the analysis of various conformational-sensitive IR bands, including CH_2 wagging, CD_2 stretching and CD_2 rocking bands. The analysis of the CH_2 wagging bands provides the relative amounts (i.e., integral numbers over the whole chain) of the *kink/gauche-trans-gauche*, *double-gauche* and *end-gauche* conformers in the tethered alkyl chains. From the analysis of the CD_2 stretching and CD_2 rocking bands information about the conformational order at a specific deuterated methylene segment is available. Here, the CD_2 rocking band data are used to determine the amount of *gauche* conformers at the deuterated carbon positions C-4 and C-6, and C-12. It is found that the conformational order critically depends on the actual alkyl chain length, chain position and sample temperature. Particular emphasis is given to the impact of the external pressure during sample preparation on the alkyl chain conformations, about which so far no information is available. It is observed that the samples prepared as KBr pellets, which experienced a pressure of about 10 kbar, are characterised by a lower amount of *gauche* conformers. This substantial increase of conformational order is attributed to better alkyl chain packing along with a gain of intermolecular chain interactions.

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1. Introduction

Alkyl-bonded silica gels are widely used as stationary phases in reverse-phase liquid chromatography, gas chromatography and solid-phase extraction for more than a decade. It is a well known fact that the alkyl chain structure and interfacial properties urge the function and utility of these stationary phase materials, and it was demonstrated that the conformational order of the alkyl chain moieties plays an important role in determining the efficiency and selectivity of separations [1–3]. Numerous investigations were performed on these kinds of stationary phase materials using a variety of experimental techniques—such as NMR [4–7], IR [8–10], Raman [11–14], fluorescence [15,16] and photo-

acoustic spectroscopy [17,18]—in order to reveal the subtleties of the alkyl chain structure. Recent studies proved that the conformational order, chain dynamics and their concomitant effects on retention and selectivity depends upon various factors such as alkyl chain lengths, surface coverage, temperature, synthetic route, etc. [19–21]. An understanding of the stationary phase behaviour under various conditions is thus crucial in order to enhance the retention mechanisms for the chromatographic separations.

As FT IR spectroscopy probes on a time scale of less than 10^{-10} s, it is perfectly suited to study the population of different conformers in quite different chemical systems. In the past, it was demonstrated that the observed absorption frequencies, intensities and band shapes critically depend on the molecular conformation, configuration and chain packing [22]. Several regions of the IR spectrum were used for the study of the alkyl chain conformational order in com-

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plex assemblies bearing hydrocarbon chains, such as self-assembled monolayers (SAMs) [23,24], model membranes, biomembranes [25] and micellar systems [26]. So far, only few FT IR studies were published about alkyl modified silica gels. Sander et al. [8] investigated a series of dimethyl-*n*-alkyl bonded phases of various alkyl chain lengths from C₁ to C₂₂ through the analysis of CH₂ stretching and CH₂ wagging modes. Recently, the influence of various parameters, like alkyl chain length, temperature and alkyl chain position, on the conformational behaviour of *n*-alkyl modified silica gels were reported for alkyl chain lengths from C₈ to C₃₀ [19,20].

In the present work, a comprehensive variable temperature FT IR study is carried out for *n*-alkyl modified silica gels in the dry state bearing selectively deuterated C₉, C₁₈ and C₂₂ alkyl chains (C_{*n*}Si-*x*, *n* = 9, 18 and 22 and *x* = 4, 6 and 12, see Fig. 1). In addition, the non-deuterated *n*-octadecyl modified silica gel is also examined. The present work addresses for the first time the effect of the sample preparation method, i.e., the influence of the sample pressure, on the conformational order of the tethered alkyl chain moieties. That is, samples were prepared by (i) placing the material directly between two KBr windows (method I, samples not subjected to pressure),

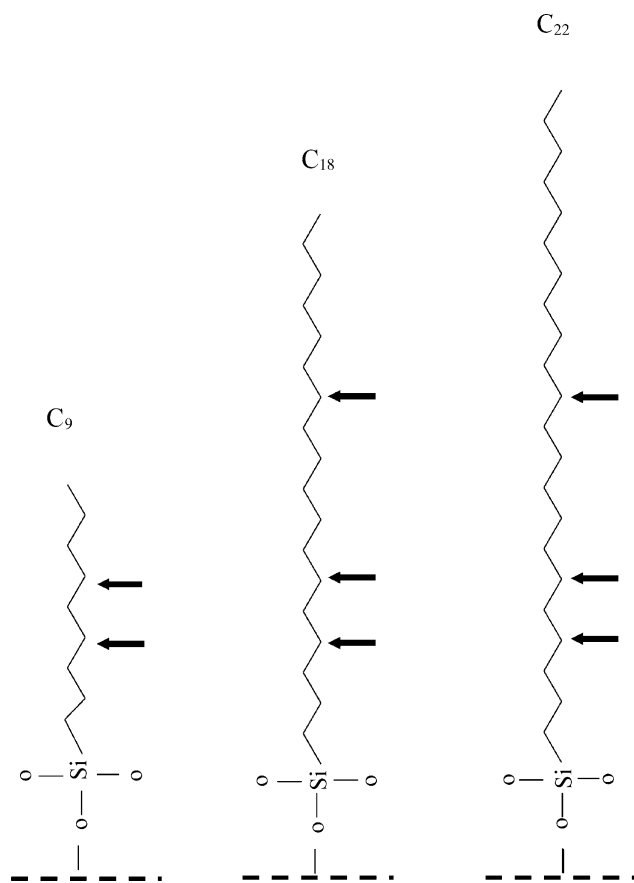


Fig. 1. Molecular structure of the selectively deuterated *n*-nonyl and *n*-octadecyl and *n*-docosyl modified silica gels. Arrows indicate the deuterated positions.

Table 1

Silane loading on a silica surface for various *n*-alkyl modified silica gels

Sample	C (%)	Surface coverage ($\mu\text{mol}/\text{m}^2$)
C ₉ Si-4	9.2	5.2
C ₉ Si-6	6.6	3.5
C ₁₈	14.3	4.2
C ₁₈ Si-4	13.8	4.0
C ₁₈ Si-6	13.9	4.1
C ₁₈ Si-12	14.1	4.2
C ₂₂ Si-4	14.8	3.6
C ₂₂ Si-6	18.4	4.8
C ₂₂ Si-12	22.0	6.2

Determined via elemental analysis; error: <2%.

and (ii) as KBr pellets (method II, external pressure of about 10 kbar during sample preparation).

Qualitative information on the conformational order is obtained via the position and widths of the CD₂ symmetric (2115–2070 cm⁻¹) and anti-symmetric stretching bands (2200–2165 cm⁻¹) [20]. Quantitative information about the average amount of *gauche* conformers within the alkyl chains is derived by the analysis of the CH₂ wagging bands. The conformational-sensitive CH₂ wagging modes appear near 1368 cm⁻¹, 1354 cm⁻¹ and 1341 cm⁻¹, which are attributed to kink/gtg, double-*gauche* (gg) and end-*gauche* (eg) sequences, respectively [27]. The CD₂ rocking vibration of selectively deuterated alkyl chains is used to probe the conformation at a particular chain position [22]. Here, the CD₂ rocking bands arising from *trans*–*trans* (tt) and *trans*–*gauche* conformations at 622 cm⁻¹ and 651 cm⁻¹, respectively, are analysed in a quantitative way in order to determine the actual amount of *gauche* conformers at the selectively deuterated chain segment.

2. Experimental

Silica gels of type 200-5-Si, i.e., silica gel with particle size of 5 μm and surface area of $S_{\text{BET}} = 200 \text{ m}^2/\text{g}$ were donated by the lab of Professor K. Albert, University of Tübingen, Germany. The non-deuterated *n*-octadecyltrichlorosilane used for the surface modifications were purchased from ABCR (Karlsruhe, Germany). The synthesis of the selectively deuterated *n*-alkyltrichlorosilanes is described elsewhere [19,20]. The deuterated and non-deuterated *n*-alkyl modified silica gels were prepared via solution polymerisation. Details about the preparation can be found in Refs. [19,20]. Carbon and hydrogen analyses were performed on a Carlo Erba Strumentazione elemental Analyser 1106 (Italy). The sample data are summarised in Table 1.

3. FT IR measurements

FT IR samples from deuterated and non-deuterated *n*-alkyl modified silica gels were prepared by two different methods. In method I, the powdered sample was placed

between two KBr windows using a 25 μm zinc spacer. In method II, pellets of modified silica gels and KBr (1/10 to 1/15 w/w) of 1 mm thickness were prepared under vacuum using a hydraulic press with a pressure of about 10 kbar; the resulting pellets were then placed in a brass cell. The cell compartment was thermostated with a variable temperature unit (L.O.T.—Oriol GmbH, Langenberg, Germany) equipped with KBr windows. The temperature setting was performed by an automatic temperature control unit with an accuracy of $\pm 0.5^\circ\text{C}$. The spectra were recorded on a Nicolet Nexus 470 FT IR spectrometer (Nicolet, Madison, WI) equipped with a DTGS detector. Typically, 256 interferograms covering a spectral range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1} were collected for temperatures ranging from 193 K to 353 K. The recorded interferograms were apodised with a triangular function and Fourier transformed with two levels of zero filling. Correction for background absorption was done by recording the background spectrum of the empty cell (measured with twice the number of interferograms as that used for the sample). The background spectrum was automatically subtracted from the respective deuterated and non-deuterated *n*-alkyl modified silica gels. Data from three independent samples were acquired at all temperatures for all the samples studied. The whole series of variable temperature FT IR spectra was measured twice for each sample. The data analysis is thus based on the average of six measurements.

4. IR data analysis

The processing and analysis of the CD_2 stretching bands were done with the OMNIC E.S.P.5.1 software (Nicolet, Madison, WI). The frequencies of the CD_2 stretching vibrations were calculated from the interpolated zero crossing in the first derivative spectra. Processing and analysis of the spectra in the CH_2 wagging region and CD_2 rocking bands were performed using the GRAMS 32 software (Galactic, Salem, NH).

For the analysis of CH_2 wagging band region, a quadratic baseline correction was applied in the spectral region of 1330–1400 cm^{-1} and for the all spectrum the same baseline points were used. The experimental spectra were fitted using four vibrational bands. Their initial positions were 1378 cm^{-1} (symmetric methyl deformation mode), 1368 cm^{-1} (kink and *gtg* sequences), 1354 cm^{-1} (double-*gauche* sequences) and 1341 cm^{-1} (end-*gauche* sequences). During the curve fit analysis, the band intensities and widths were varied independently. The integrated intensities of the CH_2 wagging bands were normalised with respect to the methyl deformation band. The amount of specific *gauche* sequences were calculated according to the procedure given in literature [28], which is based on reference measurements on alkanes and a theoretical approach using the rotational isomeric state (RIS) model [29]. The total number of *gauche* conformers per chain was obtained by taking into account that two *gauche* bonds are necessary to build up one

kink or double-*gauche* sequence. The estimated uncertainty for the various *gauche* conformers lies between 10% and 15%.

For the processing of CD_2 rocking bands, a quadratic baseline correction was applied for all samples. The CD_2 rocking band region comprises two bands, positioned at 651 cm^{-1} (*gtgt*, *gtgt* and *ttgt*) and 622 cm^{-1} (*tt*). The percentage of *gauche* bonds at a specific CD_2 segment can be calculated from the integrated intensities of these two bands, as described in Ref. [22].

5. Results and discussions

In the following, we present the results from a variable temperature FT IR study on alkyl modified silica gels in the dry state with non-deuterated C_{18} chains as well as specifically deuterated C_9 , C_{18} and C_{22} chains (deuterated positions: carbons C-4, C-6, C-12, samples $\text{C}_n\text{Si}-x$, $n=9, 18$ and 22 and $x=4, 6$ and 12 , see Fig. 1) in a range between 193 K and 353 K. Particular emphasis is given to the effect of the sample preparation method, i.e., sample pressure, on the conformational order of the tethered alkyl chains. Thus, two series of samples were examined: (i) samples which were prepared at normal pressure (method I), and (ii) samples which experienced a pressure of about 10 kbar during preparation (KBr pellet technique, method II).

In Fig. 2, a representative experimental FT IR spectrum (wagging band region between 1300 cm^{-1} and 1400 cm^{-1}) for the non-deuterated *n*-octadecyl (C_{18}) modified silica gel, prepared by method II, is shown along with the theoretical curves from the curve fitting analysis. The intense band at 1378 cm^{-1} , used as an internal reference, arises from the methyl group umbrella deformation mode. The conformational-sensitive vibrational bands appear between 1370 cm^{-1} and 1340 cm^{-1} and stem from kink/*gtg*, double-

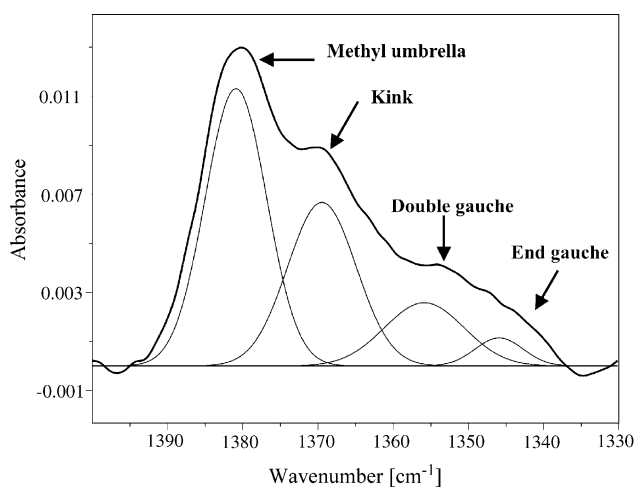


Fig. 2. Experimental FTIR spectrum (CH_2 wagging band region) bands for the C_{18} modified silica gel (method II) at 333 K. The underlying curves result from the curve fitting analysis.

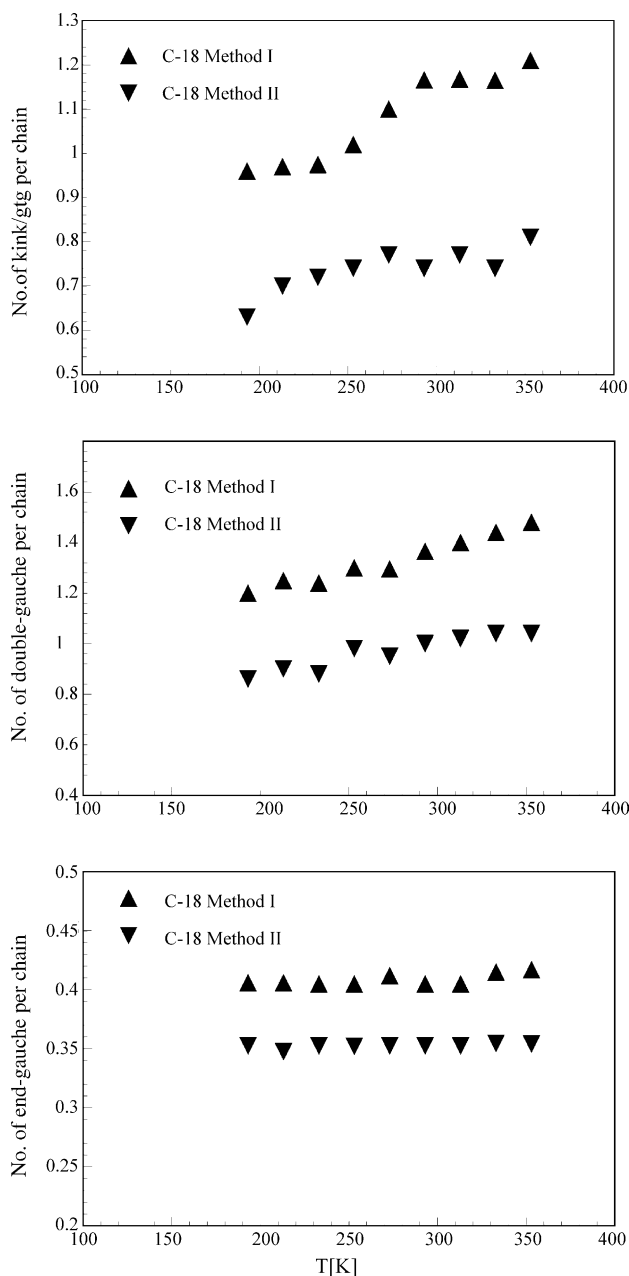


Fig. 3. Variation of kink/gtg, double-*gauche* and end-*gauche* conformers as a function of sample preparation method and temperature.

gauche and end-*gauche* sequences, respectively, as depicted in Fig. 2.

Similar FT IR spectra for *n*-octadecyl (C₁₈) modified silica gels, with emphasis on the CH₂ wagging band region, were recorded throughout a temperature range from 193 K to 353 K. The results of the CH₂ wagging band analysis for both *n*-octadecyl modified silica gel samples, which differ by their sample preparation method, are summarised in Fig. 3. An inspection of these graphs reveals a substantial increase of the amount of kink/gtg, double-*gauche* conformers per chain with increasing temperature, which holds for both preparation methods. The temperature dependence of

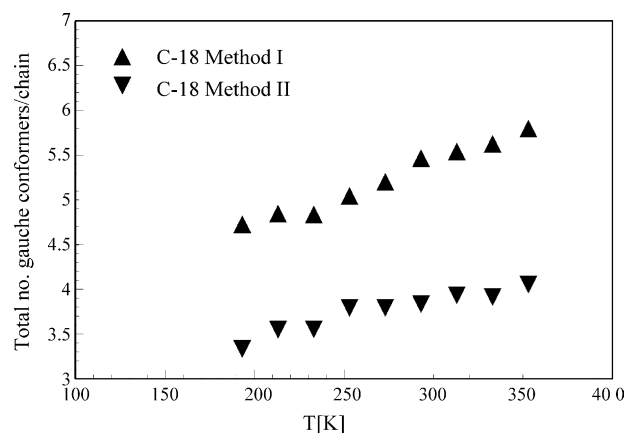


Fig. 4. Variation of total number of *gauche* conformers as a function of sample preparation method and temperature.

the kink/gtg conformers, especially above the room temperature, is somewhat more pronounced for the sample from preparation method I. Moreover, for the same sample the amount of kink/gtg conformers with values between 0.95 and 1.2 is lower than the corresponding values of 1.2–1.5 for the double-*gauche* conformers. The amount of end-*gauche* conformers per chain (about 0.4) remains almost unaffected by the actual sample temperature. It is found that the present results for the various *gauche* conformers in *n*-alkyl modified silica gels are consistent with the RIS model [29] developed for liquid alkanes, which predicts that the amount of end-*gauche* conformers is independent of the alkyl chain length, temperature and lower than the double-*gauche* and kink/gtg conformers. The total number of *gauche* conformers per chain in the *n*-octadecyl modified silica gel is depicted in Fig. 4. The total number of *gauche* conformers for method I varies between 4.7 and 5.7 in the temperature range covered here.

The impact of the actual sample preparation method, i.e., application of external pressure, on the conformational properties of *n*-octadecyl modified silica gels is clearly evident from the graphs given in Figs. 3 and 4. It can be seen that an external pressure (method II) in general increases the conformational order, as reflected by the lower amount of *gauche* conformers per chain. The relative changes are largest for the kink/gtg and double-*gauche* conformers. Moreover, it is found that the temperature dependence also is less pronounced for the sample, which experienced a high external pressure.

Similar tendencies are registered during the analysis of the CD₂ stretching and rocking bands from selectively deuterated *n*-alkyl modified silica gels, which will be presented next. The absorption frequency of the CD₂ symmetric and anti-symmetric vibration—at 2115–2070 cm⁻¹, and 2200–2165 cm⁻¹, respectively—provides qualitative information about the conformational order at the labelled methylene segment. A shift of the band maxima toward higher or lower wavenumbers thus indicates a decrease or increase of conformational order in the system of interest, respectively. A

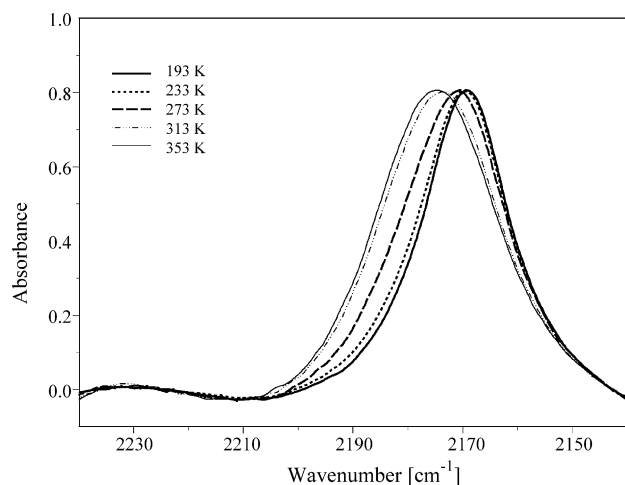


Fig. 5. Temperature dependence of the CD_2 anti-symmetric stretching modes of C_{18} modified silica gel deuterated at the position 6 ($\text{C}_{18}\text{Si-6}$), prepared by method I.

representative series of anti-symmetric stretching bands from measurements on sample $\text{C}_{18}\text{Si-6}$ is depicted in Fig. 5. The general observation is a shift of the corresponding absorption band maximum toward higher wavenumbers upon increase of the sample temperature, which points to an enhanced conformational disorder in the same direction, in close agreement with the earlier findings from the CH_2 wagging band analysis (see above). In addition, the shift of the absorption band maximum toward higher wavenumbers is accompanied by an increase of the IR bandwidth (see Fig. 5), a phenomenon which also was discussed before during IR studies on n -alkanes, phospholipids (CH_2 , CD_2 stretching bands) [30,31] and more recently in C_{30} SAMs [32]. At low temperature, the CD_2 stretching bands are narrow, reflecting relatively low acyl chain flexibility and high conformational order, whereas the increase of the CD_2 stretching bandwidth with temperature is attributed to an enhanced alkyl chain flexibility due to the decrease in conformational order.

The derived results from the analysis of the CD_2 anti-symmetric stretching bands are summarised in Fig. 6. The various graphs clearly indicate that the conformational order critically depends on the actual chain length and chain position. For instance, the absorption maxima of the n -nonyl system occur at higher wavenumbers due to a higher conformational disorder as compared to the silica gel samples with longer alkyl chain lengths. In addition, it is registered that the impact of the pressure during sample preparation on the conformational order is less pronounced in the CD_2 stretching band data.

Representative variable temperature FT IR spectra, covering the CD_2 rocking band region, for the C_{22} alkyl modified silica gels labelled at the positions C-4, C-6 and C-12 of the alkyl chains are shown in Fig. 7. These experimental spectra clearly demonstrate that the relative intensity of the vibration band at 651 cm^{-1} , characterising the *gauche* conformers, is considerably higher for chain position C-4 than for posi-

tions C-6 and C-12. These experimental FT IR spectra again prove that the actual amount of *gauche* conformers depends on both the temperature and chain position. Moreover, the comparison with the spectra from the samples with octadecyl and nonyl chains (spectra not shown) reveals a distinct chain length dependence.

The graphs in Fig. 8 depict the amount of *gauche* conformers as a function of temperature, alkyl chain length and deuterated chain position for both sample preparation methods. In Fig. 9, the percentage of *gauche* conformers is plotted against the chain position for all three n -alkyl chain lengths and for all deuterated chain positions at three selected temperatures (193 K, 273 K and 353 K). For the octadecyl chains the amount of *gauche* conformers at position C-4 (sample $\text{C}_{18}\text{Si-4}$) varies from 38% to 80% for method I, while the corresponding sample from method II exhibits only 24–40% *gauche* conformers. In agreement with the former CH_2 wagging data, the effect of temperature on the conformational order of the tethered alkyl chains is more pronounced for preparation method I (i.e., without external pressure).

The conformational order of the system with the shortest alkyl chain length (C_9) is considerably lower than for its longer counterparts. Thus, for sample $\text{C}_9\text{Si-4}$ (method I) the amount of *gauche* conformers at position C-4 is already 80% even at low temperatures, while for the sample prepared at higher pressure (method II) 70% *gauche* conformers are found. The temperature dependence, however, is different. The usual increase upon sample heating is registered for method I (89% at 353 K), while for method II the amount of *gauche* conformers decreases to 57% at elevated temperatures.

Upon moving along the alkyl chains and away from the silica surface (\rightarrow position C-6 \rightarrow position C-12), the percentage of *gauche* conformers in the octadecyl chains gradually decreases at lower temperatures or goes through a minimum at position C-6 at higher sample temperatures (see Fig. 9). The different amounts of *gauche* conformations for the chain positions C-6 and C-12 as a function of the external pressure is quite striking for both the octadecyl and docosyl modified silica gels (see Figs. 8 and 9). That is, the conformational order considerably increases upon applying an external pressure during sample preparation. In general, the conformational order of the octadecyl and docosyl modified silica gels is found to be very similar, which holds for the chain position, sample temperature and pressure dependence, although a somewhat lower amount of *gauche* conformers is registered for the latter system. These findings are in qualitative agreement with the corresponding CD_2 stretching and CH_2 wagging band data (see above).

The highest amount of *gauche* conformers is found at position C-6 in the n -nonyl modified silica gels, where 86% *gauche* conformers exist at 193 K. This value increases even further upon raising the sample temperature. It should be emphasised once again that the derived amounts of *gauche* conformers from the CD_2 rocking band analysis are in qualitative agreement with the corresponding CD_2 stretching band

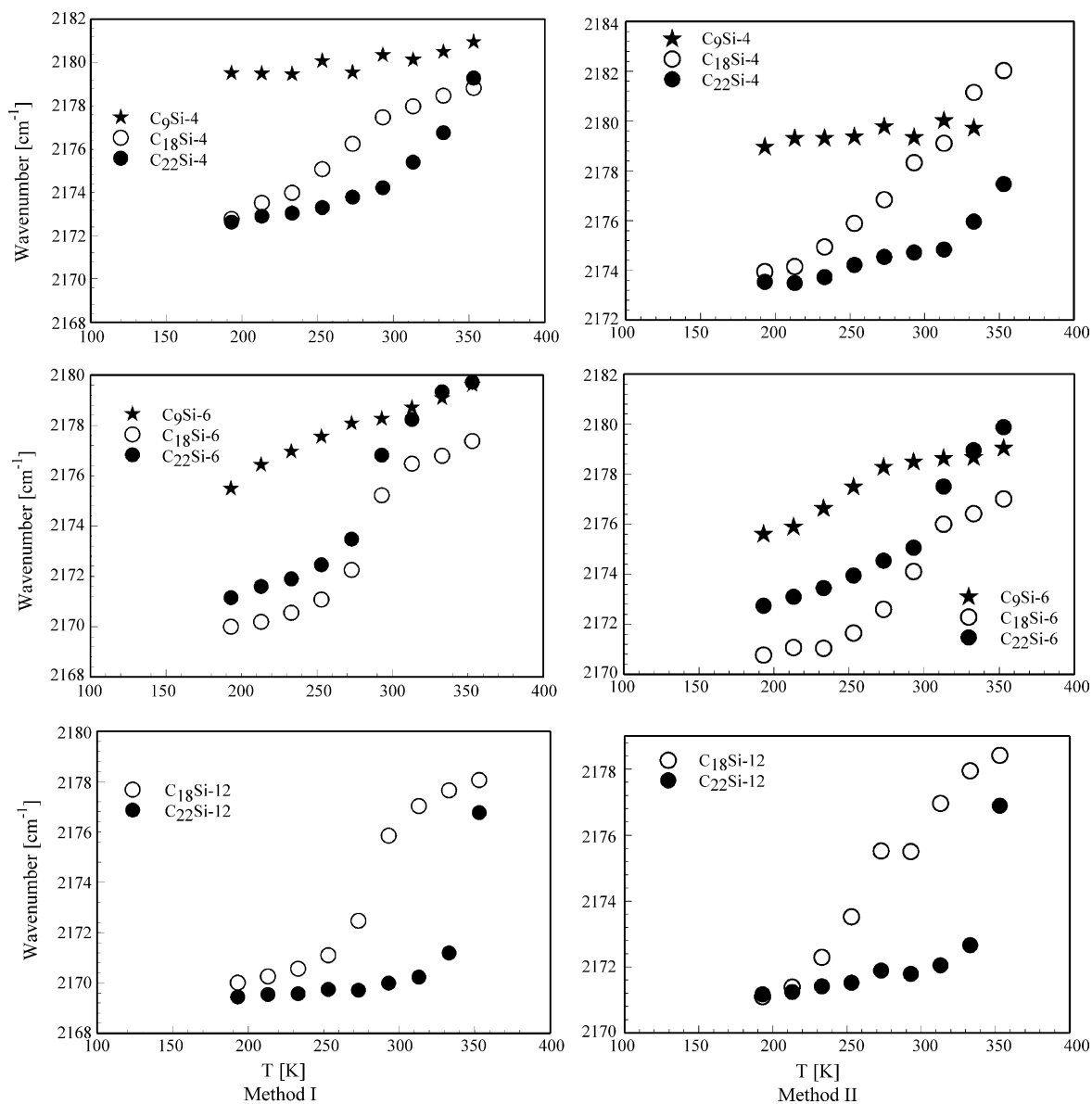


Fig. 6. Anti-symmetric CD_2 stretching band positions as a function of temperature for the selectively deuterated *n*-nonyl, *n*-octadecyl and *n*-docosyl modified silica gels.

data, which in particular holds for the position, chain length and temperature dependence, although the CD_2 stretching bands can only be considered to be a qualitative measure of the conformational order.

On the basis of present variable temperature FT IR study we can thus conclude that the conformational order of the tethered alkyl chains in chemically modified silica gels

- decreases upon raising the sample temperature,
- increases by increasing the alkyl chain length,
- increases gradually with increasing distance from the silica surface (or possesses a minimum at position C-6 at higher temperature), and
- increases upon applying pressure during sample preparation.

The present results are in agreement with former spectroscopic studies on related systems [19,20,32]. Sander et al. [8] described the application of FT IR spectroscopy to the study of the conformational order of C_1 , C_4 , C_8 , C_{12} , C_{18} , C_{22} *n*-alkyl modified silica gels by dealing with C–H stretching modes for methyl and methylene groups as well as C–H bending, scissoring and wagging modes. In these studies, a significant fraction of *gauche* conformers in the bonded *n*-alkyl chains was observed. Likewise, a Raman study on C_{18} modified silica gels from commercially available silica-based packing materials in the $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{H})$ spectral regions were performed [33]. Again, the experimental data suggested that the *n*-alkyl chains of these C_{18} modified stationary phases exist in a highly disordered state, which is similar to the case of (liquid) free *n*-alkanes. In our present work, the C_{18} modi-

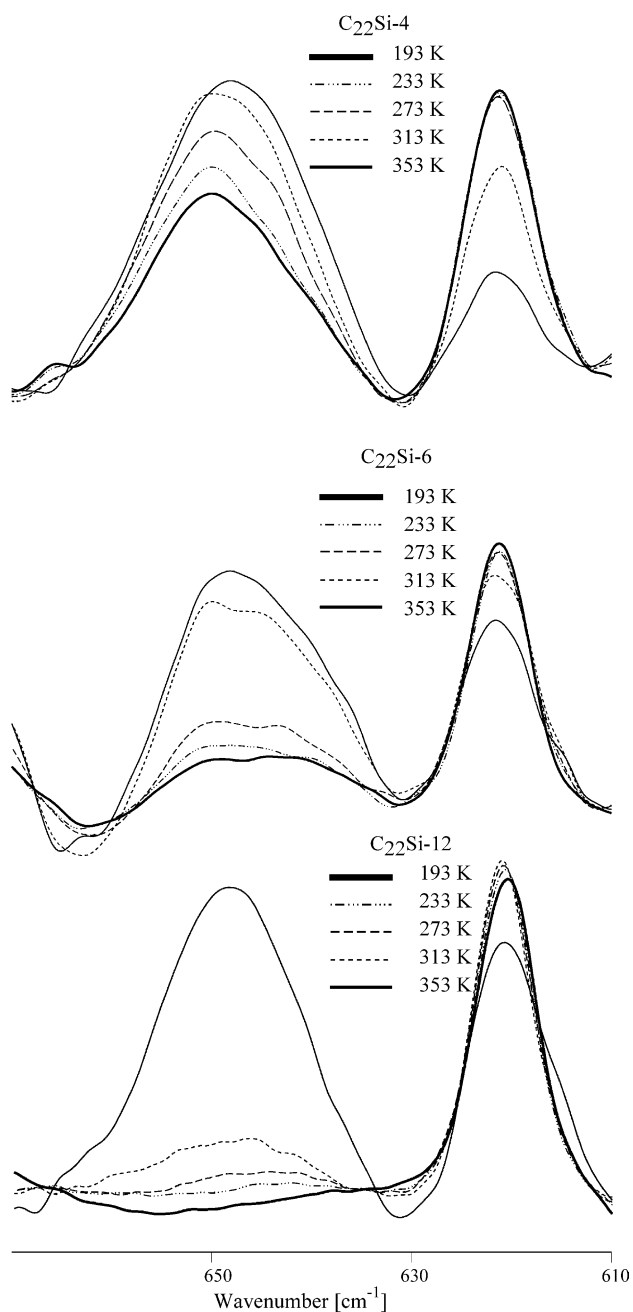


Fig. 7. Variable temperature FT IR (CD_2 rocking band region) of *n*-docosyl alkyl modified silica gels, selectively deuterated at positions C-4, C-6 and C-12 prepared by method I.

fied silica gel exhibits less conformationally disordered alkyl chains than in the corresponding free *n*-alkane, which most likely reflects the threefold higher surface coverage than that in the work by Pemberton and co-workers [33]. The surface coverage is certainly a crucial factor for the discussion of the molecular properties in such modified silica gels. A comprehensive study on the influence of this quantity on the alkyl chain conformational order is therefore in progress.

The conformational disorder in the high-temperature crystal phases of long *n*-alkanes ($\text{C}_{21}\text{H}_{44}$ and $\text{C}_{29}\text{H}_{60}$) were stud-

ied via CD_2 rocking vibrational modes [34]. It was found that the *gauche* conformers in these pure *n*-alkanes consisted entirely of kink conformations, distributed non-uniformly along the chain. The highest amount of *gauche* conformers was found at the chain ends and the concentration at interior sites decreased gradually on moving toward the centre of the chain. In the present work, *gauche* conformers were absent for *n*-docosyl modified silica gels at position C-12 at temperatures below 250 K, which is thus comparable with the findings of crystalline $\text{C}_{21}\text{H}_{44}$ at this position. In addition, it is found that the amounts of *gauche* conformers at higher temperatures in the *n*-docosyl modified silica gels are very close to those reported for $\text{C}_{21}\text{H}_{44}$ in the liquid phase [35]. Silica gels are amorphous materials and a direct comparison with the crystalline *n*-alkanes should be done with caution; in particular, it should be mentioned that in the present silica gels a calorimetric phase transition is not observed. Nevertheless, the high conformational order at low temperatures in the inner part of the *n*-docosyl chains attached to the silica surface must reflect an extremely good chain packing of this system.

Chemically modified *n*-alkyl silica gels have conformational features similar to those of surface bound *n*-alkyl chains in SAMs. Transmission IR studies for *n*-alkanethiolate SAMs on gold clusters for various *n*-alkyl chain lengths (C_3 to C_{24}) have been performed by Murray and co-workers [36]. The analysis in that work was based on the qualitative comparison of the intensity of a band, which depends on the *n*-alkyl chain length (e.g., CH_2 symmetric stretching, CH_2 wagging) with that of a band, which is invariant of the chain length (e.g., symmetric CH_3 stretching mode). Again, it was shown that for such systems shorter *n*-alkyl chains (C_3 to C_5) are highly disordered and resemble free *n*-alkanes, whereas longer chains are more conformationally ordered. It was further reported that these SAMs contain a detectable amount of *gauche* defects near the surface, which decreases with increasing chain lengths.

Recent studies on the selectively deuterated self-assembled silver *n*-octadecanethiolate layered materials also demonstrated that these materials are characterised by a lower number of *gauche* conformers in the alkyl chain near the solid surface [37]. Our present experimental data can be further compared with those from a recent study of SAMs on Au nanoparticles [23,38]. In that work, the CD_2 stretching modes of *n*-octadecanethiols deuterated at different positions [(i) positions C-2 to C-18, (ii) position C-1, and (iii) positions C-10 to C-13] bound on the surface of Au nanoparticles were analysed in order to monitor the thermally induced onset of local disorder in the *n*-alkyl chains.

The temperature dependence of the CD_2 symmetric stretching frequency of the deuterated $\text{C}_{18}\text{S}/\text{Au}$ nanoparticles confirmed that the calorimetric phase transition implicated a thermally induced change from a predominantly all-*trans* conformation to a chain disordered state. $\text{C}_{18}\text{S}/\text{Au}$ nanoparticles, whose chains have been deuterated only from the C_{10} to C_{13} , showed a much sharper disordering tran-

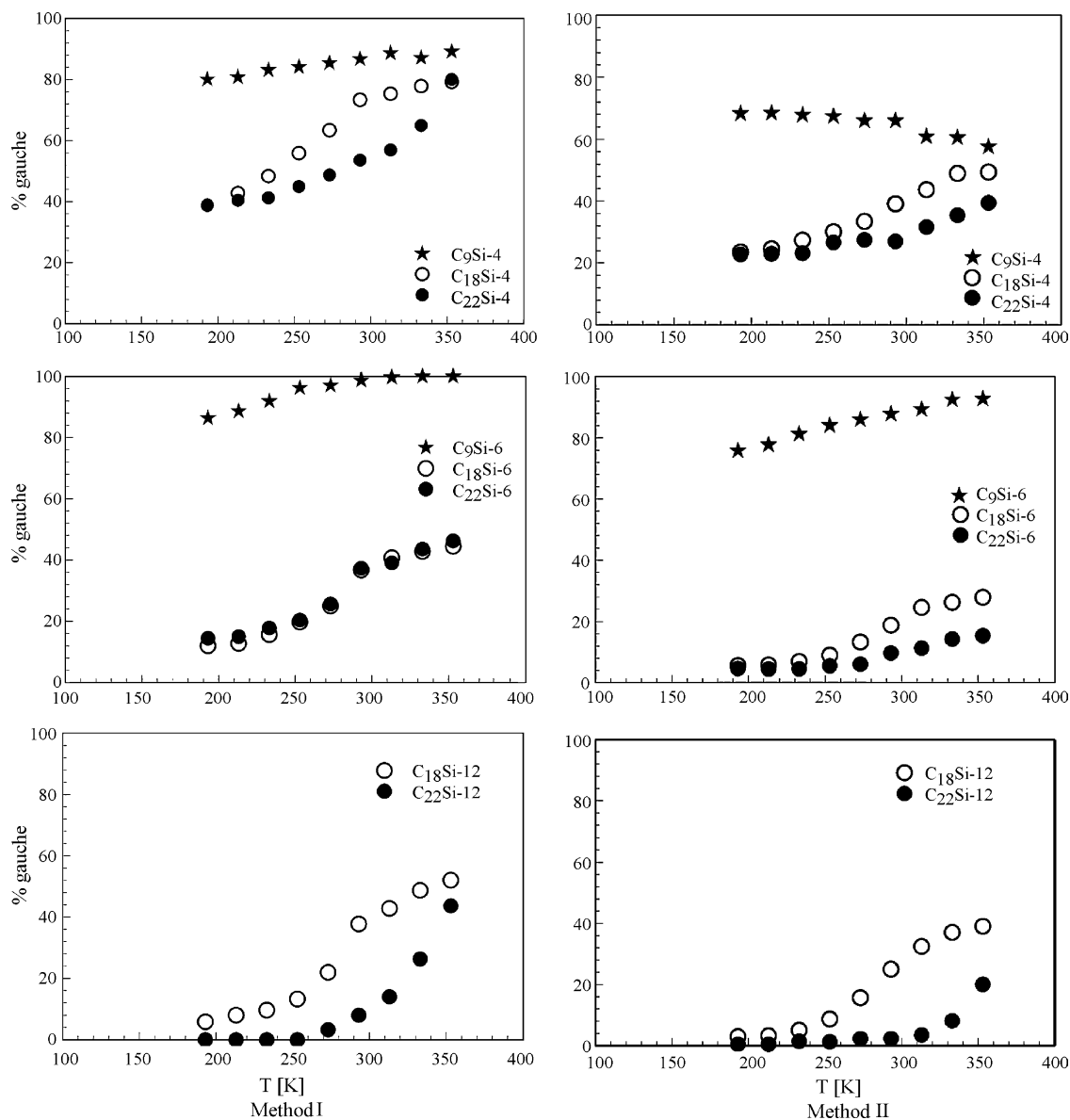


Fig. 8. Amount of *gauche* conformers at selectively deuterated positions for the *n*-nonyl, *n*-octadecyl and *n*-docosyl modified silica gels as a function of temperature.

sition than particles with perdeuterated $C_{18}SH$. Moreover, the stretching frequencies observed for $1,1-d_2-C_{18}S/Au$ did not change within the temperature range from $10^\circ C$ to $90^\circ C$, i.e., the conformational order is maintained at the carbon next to the gold surface. This strongly suggests that the conformational order decreases gradually with the distance from the solid support, and it is concluded that the chain disorder originates from the chain terminus region and propagates toward the middle of the chain as the temperature increases. This latter result is in contrast to the findings from our present work, where the methylene segments in the vicinity of the silica surface (C-4) exhibit a higher conformational disorder than the methylene groups in the inner part of the *n*-alkyl chains. It is still open whether

these differences stem from different packing densities as a result of a different surface coverage (surface coverage data are not given in Ref. [23]) or from the different nature (i.e., bond strength) of the $C_{18}S/Au$ bond. In the latter case, the chains might be able to move laterally on the gold surface. The chains then would reposition themselves to achieve optimal interaction for a low energy state along with a higher conformational order near the surface. The situation for the present alkyl modified silica gels is different, since the $\equiv Si-O-SiX_2R$ bonds are less subject to formation/reformation.

These different conformational properties of $C_{18}S/Au$, silver *n*-octadecanethiolate and *n*-alkyl modified silica gels also might reflect the use of different solid supports. In fact, the in-

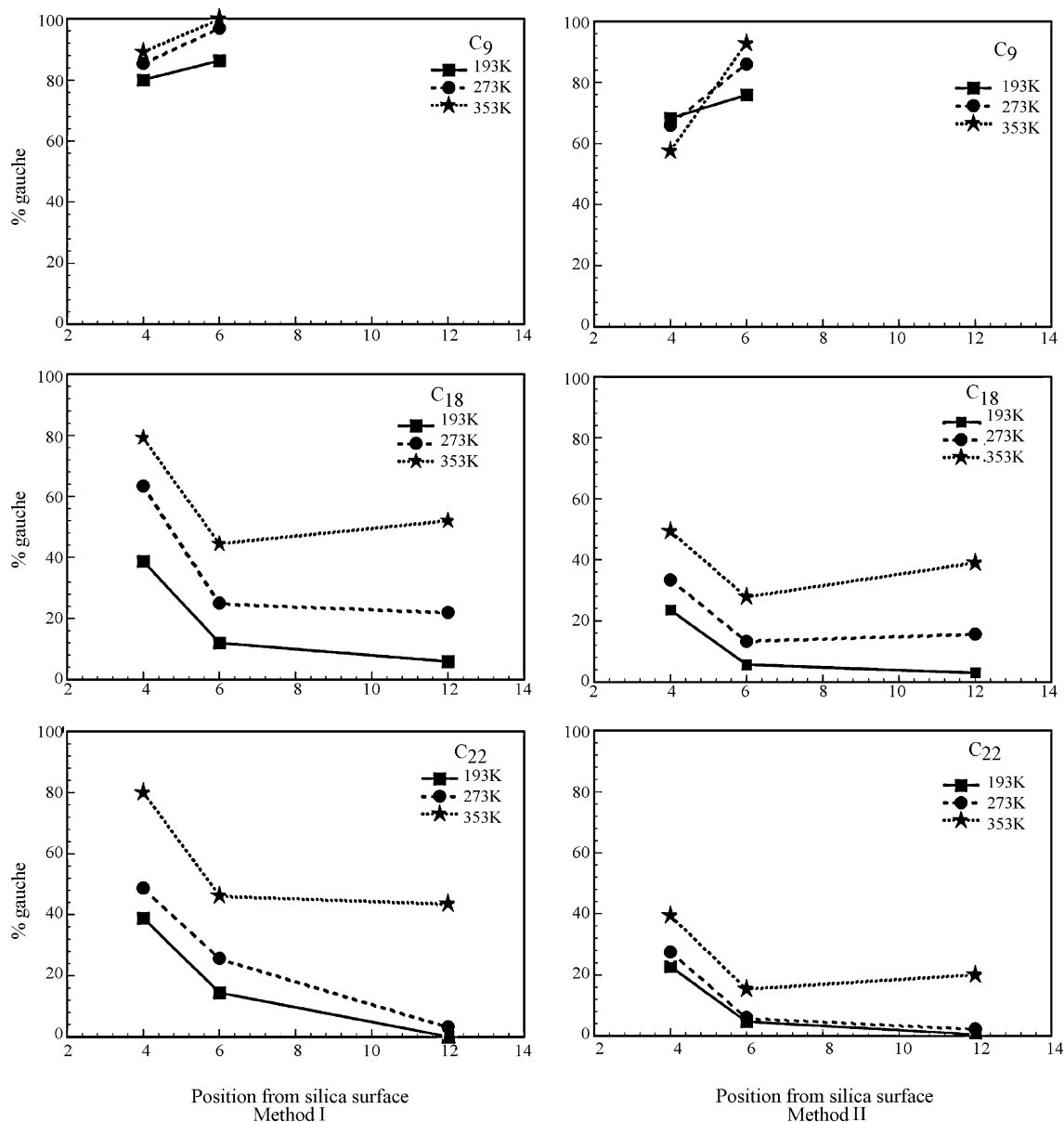


Fig. 9. The position dependence of the *gauche* amounts in *n*-alkyl modified silica gels at 193 K, 273 K and 353 K.

fluence of solid supports, like zirconia, titania and silica, on the conformational properties of C_{30} SAMs was examined recently by FT IR spectroscopy [32]. These studies clearly demonstrated that the substrate plays an important role in the conformational order of the alkyl chains that are attached to metal oxide surfaces. The comparison of the C_{30} SAMs revealed that the highest conformational order exists on titania, followed by zirconia and eventually by the silica supports. In addition, a reduced temperature dependence of the alkyl chain conformations was also derived for the C_{30} SAMs on zirconia and titania.

In a recent molecular dynamics (MD) work on modified silica gels a characteristic variation of the amount of *gauche* conformers across the alkyl chains was reported [39]. This MD simulation predicted about 17% of *gauche* conformers

at position C-4 for the C_{18} modified system at 300 K and with a similar surface coverage as used during our present work. For position C-6, a slightly larger value was reported, while the amount of *gauche* conformers increases to about 30% near the chain ends. Likewise, the lattice theory by Dill [40] predicted an increase of chain disorder with distance from the solid surface. Both results are different from our observations, where—independent of the actual preparation method—in general higher amounts of *gauche* conformers were derived, and a maximum chain disorder is found near the silica surface.

On the basis of our present FT IR investigations on *n*-alkyl modified silica gels we therefore assume that at low temperatures the inner parts (i.e., from positions C-6 up to C-12) of the C_{18} and C_{22} chains are characterised by a dense

chain packing (i.e., chain regions with high conformational order). At the same time, the methylene segments close to the silica surface—see high conformational disorder at position C-4 (CD₂ rocking data)—are conformationally disordered even at low temperatures, which might be a prerequisite for the above-mentioned packing of the inner chain segments. Moreover, in agreement with a former extensive CH₂ wagging band analysis [19] there is also a high degree of conformational freedom near the chain ends, as expressed by the high amount of end *gauche* conformers. At higher temperatures the inner chain segments gain in conformational flexibility, as can be deduced from the CD₂ stretching and rocking data. At the chain ends, i.e., beyond position C-12, the changes in conformational order with temperature were less pronounced, since here a considerable amount of conformational disorder exists (i.e., end-*gauche* conformers) even at low temperatures [19].

To our knowledge, a systematic study about the influence of pressure on the conformational properties of the tethered alkyl chains in chemically modified silica gels so far does not exist. In a recent study on monolayer-protected gold cluster molecules (MPC), different sample preparation techniques were used such as KBr pellets, dropcast films or CCl₄ solutions [41]. The corresponding FT IR spectra (symmetric and anti-symmetric CH₂ stretching bands, room temperature measurements) revealed that the conformational order of the tethered alkyl chains increases upon applying pressure during sample preparation (KBr pellets), in quite the same way as discussed for our present silica gels. Numerous studies are known which deal with pressure-induced effects on the alkyl chain conformations in the liquid phase [42,43]. Several independent studies proved that a higher sample pressure gives rise to a higher amount of *gauche* conformers, since liquid *n*-alkanes then adopt a more globular shape. This property is found to be almost independent of the actual chain length, as demonstrated by studies on *n*-hexane, *n*-pentadecane and *n*-hexadecane [44–46].

For the present chemically modified silica gels, we obviously have an opposite trend for the change of the alkyl chain conformation upon application of external pressure. The increase of conformational order with increasing pressure can be explained by an improved chain packing along with an increase of attractive intermolecular alkyl chain interactions and a more favourable overall molecular energy of the system. The chemical attachment of the alkyl chains on the solid support is certainly also very important for this characteristic change in alkyl conformational order upon sample pressure.

It is quite obvious that further studies are required in order to support this interpretation of our present experimental data. For this reason, FT IR studies are planned where the sample pressure will be changed in a more defined way. These studies will not be limited to the dry silica gels, but will also include silica gels in the presence of various solvents, a situation that is more close to the experimental condition during chromatographic separations.

6. Conclusion

A variable FT IR study has been performed in order to examine the conformational order of alkyl chains attached to silica surfaces in the dry state as a function of chain length, chain position, and sample temperature as well as external pressure during sample preparation. Through CH₂ wagging band analysis the number of kink/gtg, double-*gauche* and end-*gauche* conformers and total number of *gauche* conformers per chain were derived for the octadecyl-modified sample. It was observed that the amount of kink/gtg and double-*gauche* conformers per chain increased upon increase of temperature and decrease upon application of pressure. The analysis of the CD₂ stretching and rocking bands provides site-specific information of the conformational order. Apart from a characteristic dependence of the conformational order from the actual chain position and temperature, the amount of *gauche* conformers again is considerably reduced by application of pressure. In general, it can be concluded that the systems adopt a higher ordered conformational state upon increase of the sample pressure due to an overall gain in intermolecular chain interactions. Further studies along this line, in particular addressing the impact of the sample pressure on the molecular behaviour of such alkyl modified silica gels, are required in order to get a more detailed picture about the molecular features of these materials during the chromatographic separation.

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