Variable Temperature ^{2}H NMR and FT IR Studies of *n*-Alkyl Modified Silica Gels

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The conformational behavior of silica gels, chemically modified with selectively deuterated *n*-nonyl, *n*-octadecyl, and *n*-docosyl chains (at positions C-4, C-6, and C-12) in the dry state, were examined over a broad temperature range (123−353 K) via ^{2}H NMR and FT IR spectroscopic techniques. The aim of this study is to investigate the influence of temperature, chain length, and position on the conformational disorder and the chain dynamics in the attached *n*-alkyl chains. For this purpose the conformation-sensitive symmetric and antisymmetric stretching as well as rocking modes of selectively deuterated methylene groups were exploited. The CD$_2$ rocking band provided absolute amounts of gauche conformers at a specific site in the tethered *n*-alkyl chains. Likewise, a comprehensive ^{2}H NMR line shape analysis was performed which focused on the dynamical features of these systems. In general, it could be shown that the conformational state of the *n*-alkyl chains in fact depends on the aforementioned external parameters. Thus, the percentage of gauche conformers is found to increase with temperature, while shorter *n*-alkyl chains (i.e., *n*-nonyl systems) are more disordered than their longer counterparts (i.e., *n*-octadecyl and *n*-docosyl chains). Likewise, the effect of chain position on the order of the system is more pronounced in the longer *n*-docosyl and *n*-octadecyl chains than in the *n*-nonyl chains. The variable temperature ^{2}H NMR data were analyzed with a theoretical motional model which includes local (trans−gauche isomerization) and overall types of motion (chain reorientations). It was shown that the *n*-alkyl chain dynamics also depends on the actual *n*-alkyl chain length; that is, the *n*-nonyl chains are more mobile than the longer *n*-octadecyl and *n*-docosyl chains. The derived kinetic parameters were found to be consistent with the underlying motional models.

Introduction

During the last several years an increasing interest in the study of chemically modified silica gels has been registered, which mainly stems from their regular use in liquid chromatography and solid phase extraction processes. By far the most commonly used liquid chromatographic stationary phases are *n*-alkyl modified silica gels. For the continued development of new and useful stationary phases, it is essential to have a fundamental understanding of the conformation and dynamics of the surface bound *n*-alkyl chains. While chromatographic studies provide mostly indirect information about the bonded phase morphology,[1−4] information about the molecular structure of covalently bonded modified surfaces is perhaps best obtained through spectroscopic and scattering methods. Of these methods, NMR,[5−17] IR,[18−20] Raman,[21] fluorescence,[22−26] or photoacoustic spectroscopy[27,28] and small-angle neutron scattering[29−31] have been successfully employed in prior investigations. These studies dealt with the motional dynamics or provided evidence of the conformational disorder of the *n*-alkyl moieties.

FT IR spectroscopy is a powerful technique for probing the conformational order of *n*-alkyl chains in quite different types of chemical environments. This method has been successfully used on *n*-alkyl modified silica gels,[32] self-assembled monolayers (SAMs),[33−35] pure hydrocarbons,[36−40] and biological membranes.[41−45] Besides its ability to identify various conformational defects, FT IR spectroscopy can also be used to determine their concentration and distribution. The use of selectively deuterated *n*-alkanes as a site specific probe of

conformational defects, initially proposed by Snyder and Poore,[40] involves replacing a CH$_2$ group by a CD$_2$ group at the site of interest in the *n*-alkanes. This results in a localized CD$_2$ rocking vibration in the region between 670 and 620 cm^{-1} whose frequency is sensitive to the conformation of the two C−C bonds adjoining the CD$_2$ group. Different conformations of these bonds give rise to distinguishable bands in a region of the infrared spectrum that is free of significant interference with other vibrational modes. The frequency shift of the band maxima in the symmetric/antisymmetric CD$_2$ stretching regions (symmetric stretching, 2090−2100 cm^{-1}; antisymmetric stretching, 2195−2200 cm^{-1}) provides a qualitative measure of the changes in conformational order as a function of sample temperature or chain length and position.

Although *n*-alkyl chains have been examined earlier by solid-state NMR techniques in order to get a better understanding of the motional features of the attached *n*-alkyl chains,[6,7,11,12] several important issues, such as the effect of the chain length and chain position on the inherent chain dynamics, have not been directly addressed to date. In the following, some of the issues are addressed via a comprehensive solid state ^{2}H NMR investigation. Solid state ^{2}H NMR spectroscopy offers distinct advantages over ^{1}H and ^{13}C NMR methods for probing structure and dynamics in disordered systems. ^{2}H NMR line shapes and relaxation effects are governed by the quadrupolar interaction; that is, contributions from chemical shift anisotropy and heteronuclear dipolar interactions—as in the case of ^{1}H and ^{13}C NMR spectroscopy—can be practically neglected.[6,46−48] Moreover, the low natural abundance of the deuterium nucleus eliminates background contributions from unlabeled material so that the experimental ^{2}H NMR signal exclusively arises from

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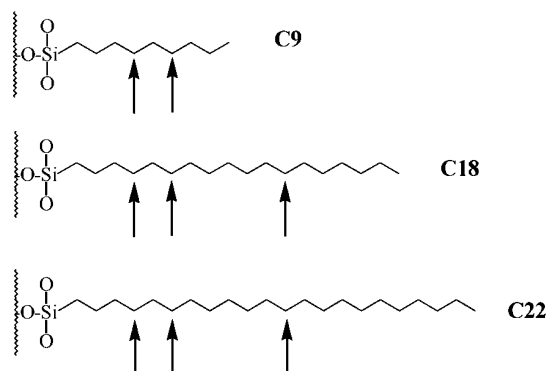
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Figure 1. Molecular structures of the selectively deuterated *n*-nonyl, *n*-octadecyl, and *n*-docosyl modified silica gels.

TABLE 1: Silane Loading on a Silica Surface for Various *n*-Alkyl Modified Silica Gels[a]

		surface density			
sample CnSi-x	% C[a]	in mg/g using RSiCl$_3$	in mg/g using RSi(OH)$_2$O	in μmol/m^2 using RSiCl$_3$	in μmol/m^2 using RSi(OH)$_2$O
C9Si-4	9.19	287.5	213.2	5.46	5.15
C9Si-6	6.61	189.6	144.9	3.60	3.50
C18Si-4	13.78	327.0	269.1	4.23	4.04
C18Si-6	13.88	329.3	271.7	4.26	4.08
C18Si-12	14.11	338.1	277.1	4.36	4.16
C22Si-4	14.83	333.6	280.8	3.74	3.60
C22Si-6	18.44	451.4	374.4	5.06	4.80
C22Si-12	22.00	589.6	483.6	6.61	6.20

[a] Determined via elemental analysis. Error: <2%.

the deuterons in the selectively labeled molecules. Since the quadrupolar interaction typically is of the order of ~170 kHz, dynamic ^{2}H NMR spectroscopy, that is, ^{2}H NMR line shape effects, can be used to probe intra- and intermolecular motions in the correlation time range between 10^{-4} and 10^{-7} s.[46,48] In the past, numerous applications have shown that an appropriate analysis of variable temperature ^{2}H NMR line shapes can provide very detailed information about the mobility (i.e., type and time scale of motion) and ordering characteristics (i.e., conformational order and overall chain order) in different types of disordered solids.[33,42] Hence, the application of FT IR and ^{2}H NMR techniques can be used to get complementary information of such systems bearing *n*-alkyl chains.

In this contribution, we report on variable temperature ^{2}H NMR and FT IR studies of silica gels, chemically modified with *n*-alkyl chains of three different lengths. The examined systems comprise *n*-nonyl, *n*-octadecyl, and *n*-docosyl chains, selectively deuterated at carbon positions C-4, C-6, and C-12 (denoted as CnSi-x with n = 9, 18, and 22 and x = the deuterated position), as shown in Figure 1. From the analysis of the above-mentioned IR vibrational bands, both qualitative (CH$_2$/CD$_2$ stretching) and quantitative (CD$_2$ rocking) information about the conformational state of these chemically modified silica gels are obtained. A quantitative analysis of the variable temperature ^{2}H NMR line shape experiments is achieved on the basis of a theoretical motional model which includes two motional contributions that occur on two different time scales. The results obtained from this study are compared with those published on other *n*-alkyl modified silica gels, pure hydrocarbons, and related systems that also contain *n*-alkyl chains in different surroundings.

Experimental Section

Synthesis and Sample Characterization. For the synthesis of the selectively deuterated *n*-alkyltrichlorosilanes, LiAlD$_4$, methyl nonadecanoate, methyl heptadecanoate, ethyl undecanoate, ethyl butyrate, and the corresponding alkenyl bromides (allyl bromide, pent-4-enyl bromide, or undec-10-enyl bromide) were purchased from either Acros or Aldrich Chemicals (Steinheim, Germany). Toluene was used without further purification. THF and diethyl ether were distilled with Na-benzophenone and CaH$_2$, respectively, prior to use. Carbon and hydrogen analyses were performed on a Carlo Erba Strumentazione elemental analyzer 1106 (Italy).

The general synthesis of the selectively deuterated *n*-alkyltrichlorosilanes and the corresponding modified silica gels was already described elsewhere.[32] Therefore, the basic procedures are only briefly summarized here.

Synthesis of Deuterated *n*-Alkyltrichlorosilanes. In the following the synthesis of a selectively deuterated *n*-docosene

is exemplarily given. The first step involved the preparation of the selectively deuterated *n*-alkenes. This was achieved by the reduction of a carboxylic ester with an appropriate chain length (for example, C$_{10}$H$_{21}$COOCH$_3$) with LiAlD$_4$ in order to get a selectively deuterated alcohol (for example, C$_{10}$H$_{21}$CD$_2$OH). Then, the alcohol was brominated and the Grignard reagent of the resulting bromide was coupled with an appropriate alkenyl bromide (for example, undec-10-enyl bromide) in the presence of CuCl$_2$/LiCl catalyst to yield the desired selectively deuterated *n*-alkene (for example, docosene-12,12-d_2). In the final step, the selectively deuterated *n*-alkene was reacted with trichlorosilane in the presence of hexachloroplatinic(VI) acid (H$_2$PtCl$_6$) as catalyst to give the desired selectively deuterated *n*-alkyltrichlorosilanes[16] in THF. The reaction mixture was stirred for 20 h at room temperature. Then unreacted trichlorosilane and THF were removed under vacuum.

Synthesis of *n*-Alkyl Modified Silica Gels.[49,51] Preactivated silica gel (type 200-5-Si, i.e., silica gel with particle size 5 μm and surface area S_{BET} = 200 m^2/g) was suspended in toluene, heated to 80 °C, and was stirred with a 2-fold excess of the corresponding selectively deuterated *n*-alkyltrichlorosilane [C$_n$H$_{2n-1}$D$_2$Cl$_3$Si with n = 9, 18, or 22]. Addition of a small amount of water initiated the solution polymerization reaction (see original procedure in refs 49 and 50). After the suspension was stirred at reflux with a KPG stirrer for about 2 days, the modified silica gel was filtered and washed with toluene and subsequently with methanol and petroleum ether. The filtered *n*-alkyl modified silica gel was dried under vacuum and was stored in airtight bottles.

Characterization of the prepared sample was performed via ^{13}C and ^{29}Si CP/MAS NMR spectroscopy[10] and elemental analysis.[52,53] The surface densities α_{RP}[52,53] of the present samples, as summarized in the Table 1, were calculated with eq 1.

$$\alpha_{RP} = \frac{10^6 P_C}{1200 n_C - P_C(M - n_x)} \frac{1}{S_{BET}} \; (\mu\text{mol/m}^2) \quad (1)$$

P_C is the percentage of carbon determined via elemental analysis, n_C is the number of carbon atoms per silane moiety, M is the molar mass of the silane (see Table 1), n_x is the number of reactive groups in the silane (n_x = 3 for *n*-alkyltrichlorosilane), and S_{BET} (=200 m^2/g) is the specific surface area of the unmodified support.

FT IR Measurements. *Sample Preparation and Variable Temperature Measurements.* Pellets (1 mm thick) of modified silica gels and KBr (1:10 to 1:15 w/w) were prepared under vacuum using a hydraulic press. These pellets were placed in a brass cell equipped with an external thermocouple in close

vicinity to the sample. The same thermocouple was also used for monitoring the actual sample temperature. The brass cell was thermostated in a variable temperature transmission cell (L. O. T.—Oriel GmbH, Langenberg, Germany), equipped with NaCl windows. The temperature was regulated with an automatic temperature control unit. The temperature accuracy was estimated to be ±0.5 °C.

IR Measurements. FT IR spectra between 123 and 353 K were recorded on a Nicolet Nexus 470 FT IR spectrometer (Nicolet, Madison, WI) equipped with a DTGS detector. Each spectrum is an average of 512 interferograms, covering a spectral range from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1}. The recorded interferograms were apodized 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 subsequent spectra of *n*-alkyl modified silica gels. Data from three independent samples were acquired at all temperatures for all samples studied. The whole series of variable temperature spectra was measured twice for each sample. The data analysis is thus based on an average of six measurements.

IR Data Analysis. The processing and analysis of the spectra in the CD_2 rocking regions were performed with the aid of the Grams/32 software package (Galactic, Salem, NH), whereas the CH_2/CD_2 stretching band analysis was done with the OMNIC E.S.P.5.1 software package (Nicolet, Madison, WI). The frequencies of the CD_2 and CH_2 stretching vibrations were determined from the interpolated zero crossing in the first derivative spectra without a baseline correction of the original IR spectra.

A quadratic baseline correction was applied to the CD_2 rocking region (670−610 cm^{-1}) prior to further spectral analysis. Here, curve-fitting methods were used to determine the band intensities of the conformation-sensitive bands. For the CD_2 rocking band analysis, the two IR main bands were initially placed at 651 cm^{-1} (gtgt, g'tgt, ttgt) and 622 cm^{-1} (tt). Line widths and intensities of the four input vibrational bands were allowed to vary during computation. The integral intensities of these two bands after iteration were used to calculate the percentage of the gauche bonds at the specific position in the *n*-alkyl segment, employing eq 2.[44] The estimated uncertainty in analysis of the gauche conformer is 10−15%.

$$\% \text{ gauche} = \frac{I(651 \text{ cm}^{-1})}{2I(622 \text{ cm}^{-1}) + I(651 \text{ cm}^{-1})} \quad (2)$$

^{2}H NMR Spectroscopy. *^{2}H NMR Measurements and Data Processing.* ^{2}H NMR experiments between 140 and 360 K were performed at 46.07 MHz on a CXP 300 spectrometer interfaced with a Tecmag spectrometer control system using the quadrupole echo sequence[54−56] $(\pi/2)_x−\tau_e−(\pi/2)_y−\tau_e−$acquisition, with a $\pi/2$ pulse length of 2.0 μs and a pulse spacing of $\tau_e = 20$ μs. Recycle delays were chosen to be at least 10 times the spin−lattice relaxation times (300 ms to 1 s). The number of scans typically was 10240. The sample temperature was controlled with a Bruker BVT 1000 temperature control unit. To have the exact sample temperature, an external temperature calibration was performed prior to the NMR measurements by putting a thermocouple in the NMR sample coil. The temperature stability was found to be within ±1 K. The data processing of the experimental and simulated NMR signals was performed on SUN Sparc 10 workstations using NMRi and Sybyl software packages (Tripos, St. Louis, MO).

TABLE 2: Variable Parameters Used for Theoretical ^{2}H NMR Line Shapes of the *n*-Nonyl Modified Silica Gels[a]

	C9Si-4			C9Si-6		
T (K)	τ_w (s)	τ_{t-g} (s)	% gauche	τ_w (s)	τ_{t-g} (s)	% gauche
160	10^{-5}	10^{-6}	20	10^{-6}	10^{-7}	30
180	10^{-6}	10^{-7}	30	9×10^{-7}	10^{-7}	40
200	5×10^{-7}	10^{-7}	30	10^{-7}	10^{-7}	40
220	3×10^{-7}	10^{-7}	30	10^{-7}	$\leq 10^{-8}$	40
240	10^{-7}	10^{-7}	40	$\leq 10^{-8}$	$\leq 10^{-8}$	60
260	10^{-7}	$\leq 10^{-8}$	40	$\leq 10^{-8}$	$\leq 10^{-8}$	70
280	$\leq 10^{-8}$	$\leq 10^{-8}$	40	$\leq 10^{-8}$	$\leq 10^{-8}$	70
300	$\leq 10^{-8}$	$\leq 10^{-8}$	40	$\leq 10^{-8}$	$\leq 10^{-8}$	70

[a] Estimated errors for the amount of gauche conformers are ≤25% for the high temperature range ($T \geq 240$ K) and ≤50% for the low temperature range; estimated errors are 1 order of magnitude for the correlation time τ_{t-g} (trans−gauche isomerization), and half an order of magnitude for the correlation time τ_w (chain wobbling).

^{2}H NMR Line Shape Simulation and Motional Model. The theoretical simulations presented in the current work were done with appropriate FORTRAN programs that describe the behavior of an $I = 1$ nuclear spin undergoing various types of motions, developed in our group.[57,58] For the line shape simulations, a slow-motional[58,59] approach was used. The approach assumes infinitesimal sharp rf pulses and explicitly accounts for the interval τ_e in the quadrupole echo experiment, being responsible for spin−spin relaxation. During the present work, the following constant simulation parameters were used: quadrupolar coupling constant = 167 kHz, line broadening = 3 kHz, sweep width = 1 MHz, number of points in FID = 512, and pulse spacing τ_e = 20 μs. All other (variable) parameters, that is, motional correlation times and amount of gauche conformers, are summarized in Tables 2−4. To reproduce the experimental line shapes, various motional models were tested. Numerous theoretical simulations have shown that the best reproduction of the experimental ^{2}H NMR spectra can be achieved by considering two superimposed motional contributions, namely 32-site (overall) wobbling of the chains along with a (local) 2-site trans−gauche isomerization process. Basically the present 32-site model is an extension of the 19-site wobbling model proposed by Vold et al.[60] Thus, we subdivided a sphere into seven layers, where θ is the opening angle of the cone that is defined by each layer (see Figure 2a). The number of sites n_{site} of the various layers is given by 1, 3, 6, 12, 6, 3, and 1 at the opening angles $\theta = 0°, 30°, 60°, 90°, 120°, 150°$, and $180°$, respectively. The motional exchange was allowed to take place only between the neighboring sites or between the adjacent planes (see Figure 2b). In principle, the populations of both the wobble sites and the isomerization states could be varied. For the present silica gels the populations of the wobble sites in each layer (or plane), however, were kept constant according to eq 3,

$$p_i = \frac{\sin \theta_i}{\sum \sin \theta_i n_{site}} \quad (3)$$

Here, p_i and n_{site} are the population of a site i and the number of sites in a particular plane, respectively.

Prior to the final ^{2}H NMR line shape fitting, a series of the model calculations were performed in order to examine the influence of the amount of gauche conformers as well as the correlation times for trans−gauche isomerization and chain wobbling on the theoretical ^{2}H NMR line shapes. These theoretical simulations were then further refined until eventually a satisfactory agreement between experiment and simulation was achieved.

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TABLE 3: Variable Parameters Used for Theoretical ^{2}H NMR Line Shapes of the *n*-Octadecyl Modified Silica Gels[a]

	C18Si-4			C18Si-6			C18Si-12		
T (K)	τ_w (s)	τ_{t-g} (s)	% gauche	τ_w (s)	τ_{t-g} (s)	% gauche	τ_w (s)	τ_{t-g} (s)	% gauche
160	$\geq 10^{-3}$	$\geq 10^{-3}$	0	$\geq 10^{-3}$	$\geq 10^{-3}$	0	$\geq 10^{-3}$	$\geq 10^{-3}$	0
180	$\geq 10^{-3}$	4×10^{-6}	10	$\geq 10^{-3}$	4×10^{-6}	10	$\geq 10^{-3}$	5×10^{-6}	10
200	$\geq 10^{-3}$	10^{-6}	20	$\geq 10^{-3}$	10^{-6}	20	$\geq 10^{-3}$	3×10^{-7}	30
220	10^{-4}	10^{-7}	30	5×10^{-6}	10^{-7}	30	10^{-4}	10^{-7}	30
240	8×10^{-7}	10^{-7}	30	2×10^{-6}	10^{-7}	30	2×10^{-6}	$\leq 10^{-8}$	30
260	3×10^{-7}	10^{-7}	30	7×10^{-7}	10^{-7}	40	3×10^{-7}	$\leq 10^{-8}$	30
280	10^{-7}	$\leq 10^{-8}$	38	10^{-7}	$\leq 10^{-8}$	40	$\leq 10^{-8}$	$\leq 10^{-8}$	40
300	5×10^{-8}	$\leq 10^{-8}$	40	$\leq 10^{-8}$	$\leq 10^{-8}$	40	$\leq 10^{-8}$	$\leq 10^{-8}$	70

[a] For estimated errors, see Table 2.

TABLE 4: Variable Parameters Used for Theoretical ^{2}H NMR Line Shapes of the *n*-Docosyl Modified Silica Gels[a]

	C22Si-4			C22Si-6			C22Si-12		
T (K)	τ_w (s)	τ_{t-g} (s)	% gauche	τ_w (s)	τ_{t-g} (s)	% gauche	τ_w (s)	τ_{t-g} (s)	% gauche
160	10^{-4}	10^{-4}	10	$\geq 10^{-3}$	$\geq 10^{-3}$	10	$\geq 10^{-3}$	10^{-4}	10
180	10^{-4}	10^{-7}	20	$\geq 10^{-3}$	10^{-6}	10	$\geq 10^{-3}$	3×10^{-6}	10
200	10^{-5}	10^{-7}	20	10^{-4}	10^{-6}	10	10^{-4}	10^{-6}	10
220	8×10^{-6}	10^{-7}	30	10^{-4}	10^{-7}	20	10^{-5}	10^{-7}	30
240	3×10^{-6}	10^{-7}	30	2×10^{-6}	10^{-7}	30	2×10^{-6}	10^{-7}	30
260	10^{-6}	10^{-7}	30	10^{-6}	$\leq 10^{-8}$	30	10^{-6}	10^{-7}	33
280	6×10^{-7}	10^{-7}	30	3×10^{-7}	$\leq 10^{-8}$	30	7×10^{-7}	10^{-7}	40
300	3×10^{-7}	10^{-7}	40	$\leq 10^{-8}$	$\leq 10^{-8}$	40	3×10^{-7}	10^{-7}	50

[a] For estimated errors, see Table 2.

Results

FTIR Spectroscopy. *CH_2 Symmetric Stretching Band Analysis.* The CH_2 stretching mode can be utilized to discuss the evolution of the conformational order in the polymethylene segments, for instance as a function of the sample temperature or in the vicinity of phase transitions. Hence, the position of the CH_2 stretching band in the region between 2849 and 2854 cm^{-1} provides a qualitative measure of the conformational disorder. A higher wavenumber of this vibration band thus is known to reflect a higher conformational disorder in the system of interest.[36] Figure 3 shows the derived data for the CH_2 symmetric stretching bands as a function of temperature. It can be seen that, upon increasing the sample temperature, the corresponding absorption band maxima for all samples—independent of *n*-alkyl chain length—are shifted toward higher wavenumbers. The position of the band maximum, as well as the actual temperature dependence, varies with the sample, that is, with the *n*-alkyl chain length. According to these curves, the shorter chains in the *n*-nonyl modified system are therefore conformationally more disordered than their two longer counterparts (C18 and C22).

CD_2 Rocking Band Analysis. The analysis of the CD_2 rocking vibrational bands between 600 and 680 cm^{-1} provides the amount of gauche conformers at a specific site in a polymethylene segment. It is based on the sensitivity of the rocking mode frequency of an isotopically isolated CD_2 group to the conformation of the two C—C bonds adjacent to the CD_2 group.[44] Representative IR rocking band spectra are given in Figures 4 and 5. They refer to the five different silica gels with selectively deuterated *n*-docosyl and *n*-nonyl chains. The corresponding FT IR spectra of the silica gels with *n*-octadecyl chains, that are not given here, are very similar to those of the *n*-docosyl system. It can be seen that all silica gel samples exhibit two absorption bands at 622 and 651 cm^{-1}, which—as outlined earlier (see Experimental Section)—stem from trans and gauche conformers, respectively. Obviously, at about room temperature for the long *n*-alkyl chain systems (C18, C22), the relative intensity of the gauche vibrational band at 651 cm^{-1} is highest for samples C22Si-4 and C18Si-4, where the deuterated methylene segment is located closer to the silica surface, whereas for samples C22Si-6, C18Si-6 and C22Si-12, C18Si-12 a much weaker intensity of this specific band is registered. For *n*-nonyl modified silica gels (see Figure 5) the situation is quite different. Here, in general, the intensity of the gauche peak is substantially higher than that of the corresponding trans signal, which holds for both samples (C9Si-4 and C9Si-6) throughout the whole temperature range covered here.

From a curve fitting procedure (see Experimental Section) the percentage of gauche conformers was derived for all deuterated chain positions in the various *n*-alkyl chains of different chain lengths. Inspection of the various plots, given in Figure 6, clearly demonstrates that the conformational order is strongly affected by the particular chain length, chain position, and sample temperature. Except for the case of the sample C9Si-4, there is always a trend toward a higher gauche content if the sample temperature is increased. Likewise, for the longer *n*-alkyl chains (C18 and C22) a gradual decrease of the gauche content from carbon position C-4 via C-6 to position C-12 is registered. Finally, an increase of the *n*-alkyl chain length gives rise to a reduced amount of gauche conformers (i.e., higher conformational order), which is found to be independent of the labeled chain position.

CD_2 Stretching Band Analysis. The symmetric and antisymmetric CD_2 stretching band positions of selectively deuterated *n*-alkyl chains are qualitative markers of the conformational state at a particular labeled chain segment and can be used as additional support of the CD_2 rocking data. In Figure 7 the positions of the CD_2 antisymmetric stretching band maxima are plotted as a function of temperature for the various selectively deuterated silica gels. A comparison of these plots reveals a close resemblance to the aforementioned amounts of gauche conformers from the analysis of CD_2 rocking band data, as displayed in Figure 6. As before, three general trends can be derived from these CD_2 stretching data: (i) shorter chains exhibit absorption maxima at higher wavenumbers, (ii) a shift toward higher wavenumbers is registered upon increasing the sample temperature, and (iii) the wavenumbers strongly depend on the actual chain position. This close resemblance of
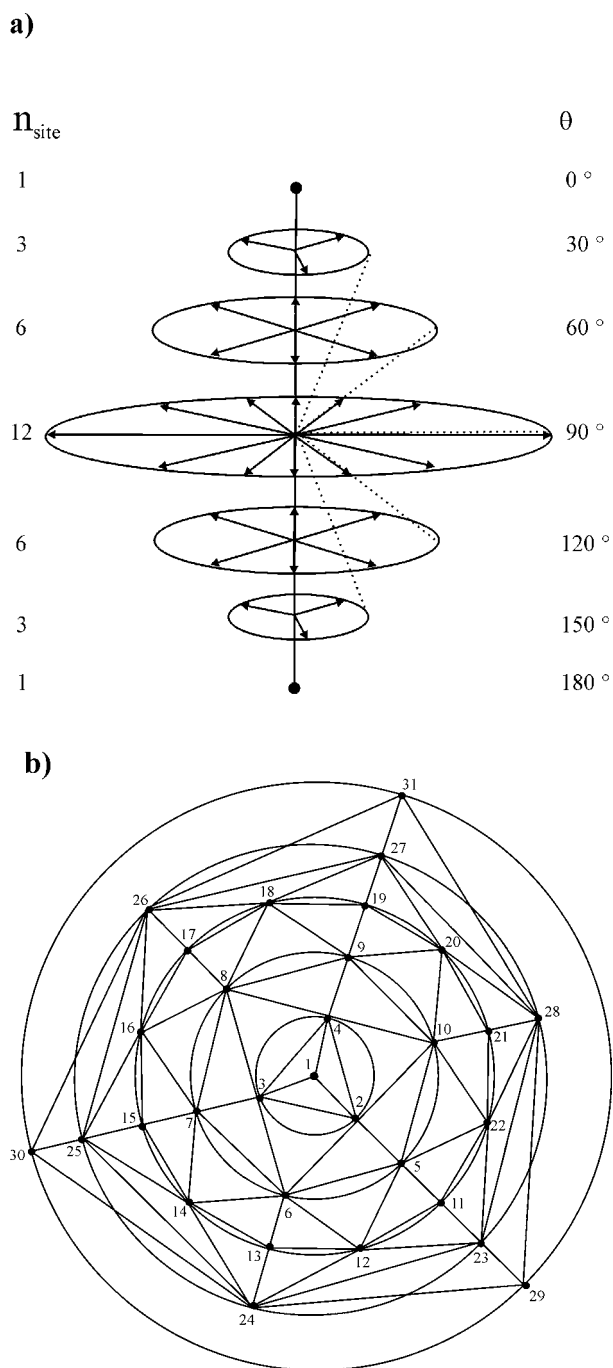
a)

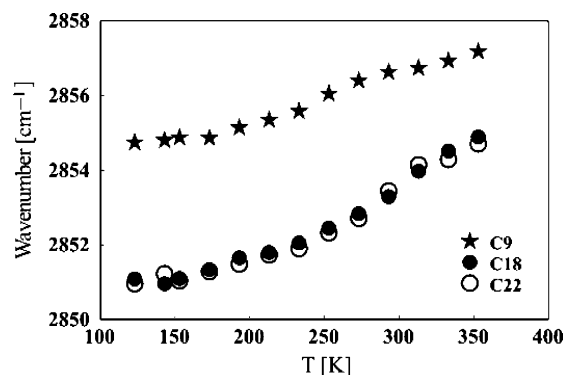**Figure 3.** Symmetric CH$_2$ stretching band positions in *n*-nonyl, *n*-octadecyl, and *n*-docosyl modified silica gels.

b)

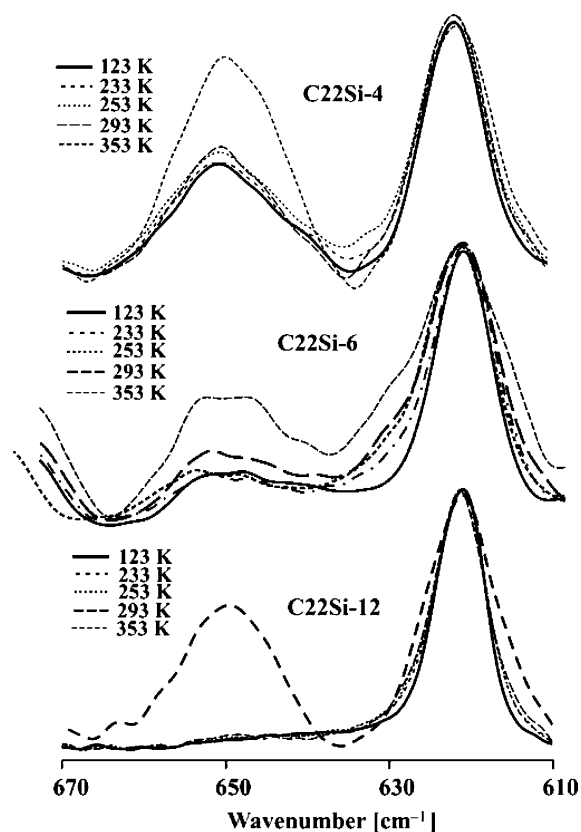**Figure 2.** (a) Schematic diagram of the 32-site wobble model. θ is the opening angle of the cone that is defined by each layer. n_{site} is the number of sites in each layer. (b) Site designation for the 32-site wobble model and exchange pathways. The 32nd site, connected to sites 29, 30, and 31, is not shown.

the CD$_2$ rocking and CD$_2$ stretching data is further demonstrated by the graphs in Figure 8 where for the *n*-docosyl system the positions of the CD$_2$ stretching band maxima are plotted against the ratios $I(651)/[I(651) + 2I(622)]$ from the CD$_2$ rocking band data. Similar correlation curves can also be found for the *n*-nonyl and *n*-octadecyl systems (data not shown).

^{2}H NMR Spectroscopy. *^{2}H NMR Line Shapes.* IR measurements are essentially a snapshot of the different bond conformations—and thus of chain disorder—in a given area of irradiation. ^{2}H NMR spectroscopy provides insight into the motional processes which accompany the chain disordering.

Figure 4. Variable temperature FT IR spectra (CD$_2$ rocking band region) of C22 modified silica gels, deuterated at positions C-4, C-6, and C-12.

Representative variable temperature ^{2}H NMR line shapes of the present *n*-alkyl modified silica gels are shown in Figure 9. At low temperatures ($T < 180$ K), except for the case of C9Si-6, for all samples a spectrum close to the static Pake pattern with a splitting between 120 and 123 kHz is observed, indicating little or no motion of the C—D bonds in the *n*-alkyl chains attached to the solid silica support. At higher temperatures the experimental ^{2}H NMR spectra are altered due to onset of thermally activated molecular motions. In fact, at sufficiently high temperatures a considerable narrowing of the experimental line shapes is registered ($T > 200$ K for *n*-octadecyl and *n*-docosyl, $T > 160$ K for C9Si-6, and $T > 140$ K for C9Si-4). Obviously, the spectral narrowing occurs at lower temperatures for the shorter *n*-nonyl chains than for the longer *n*-octadecyl and *n*-docosyl chains. In a more quantitative way, this can be shown by the full width at the half-height (fwhh), which is plotted in Figure 10 as a function of temperature. For the
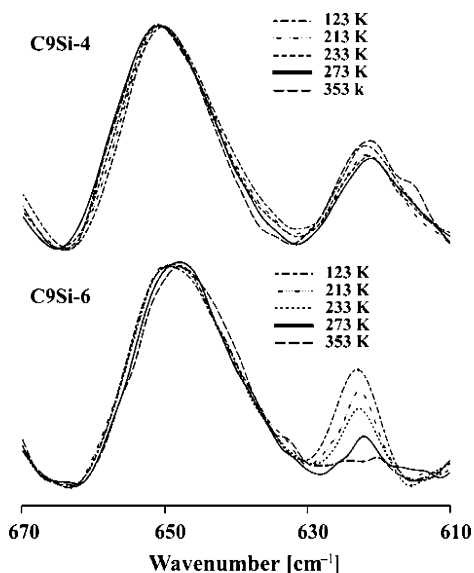
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Figure 5. Variable temperature FT IR spectra (CD$_2$ rocking band region) of C9 modified silica gels, deuterated at positions C-4 and C-6.
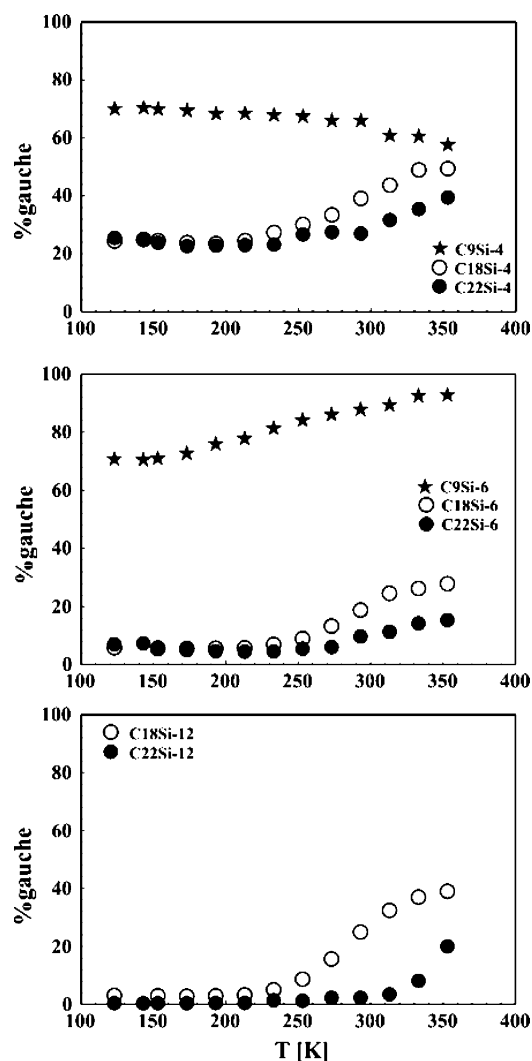

Figure 6. Amount of gauche conformers at specific chain positions for deuterated *n*-nonyl, *n*-octadecyl, and *n*-docosyl modified silica gels.

Figure 7. Antisymmetric CD$_2$ stretching band positions for the selectively deuterated *n*-nonyl, *n*-octadecyl, and *n*-docosyl modified silica gels.
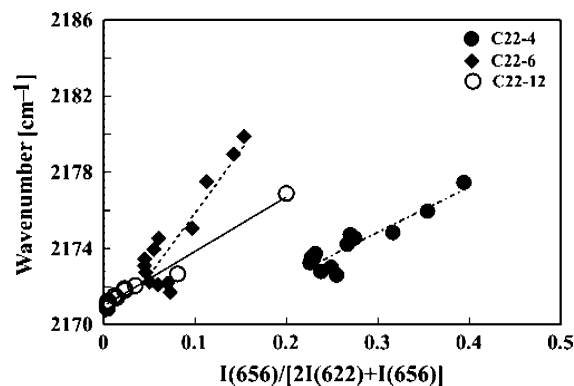

Figure 8. Antisymmetric CD$_2$ stretching band positions plotted against CD$_2$ rocking data for selectively deuterated *n*-docosyl modified silica gels.

n-octadecyl and *n*-docosyl systems the fwhh remains fairly constant with values between 110 and 130 kHz from 160 to 250 K. At about 250 K the spectral width decreases rapidly,

reaching values between 15 and 30 kHz for the *n*-octadecyl and 10 and 25 kHz for the *n*-docosyl modified silica gels, where smaller values are found for the methylene segments that are farther apart from the silica surface (i.e., C-6 and C-12
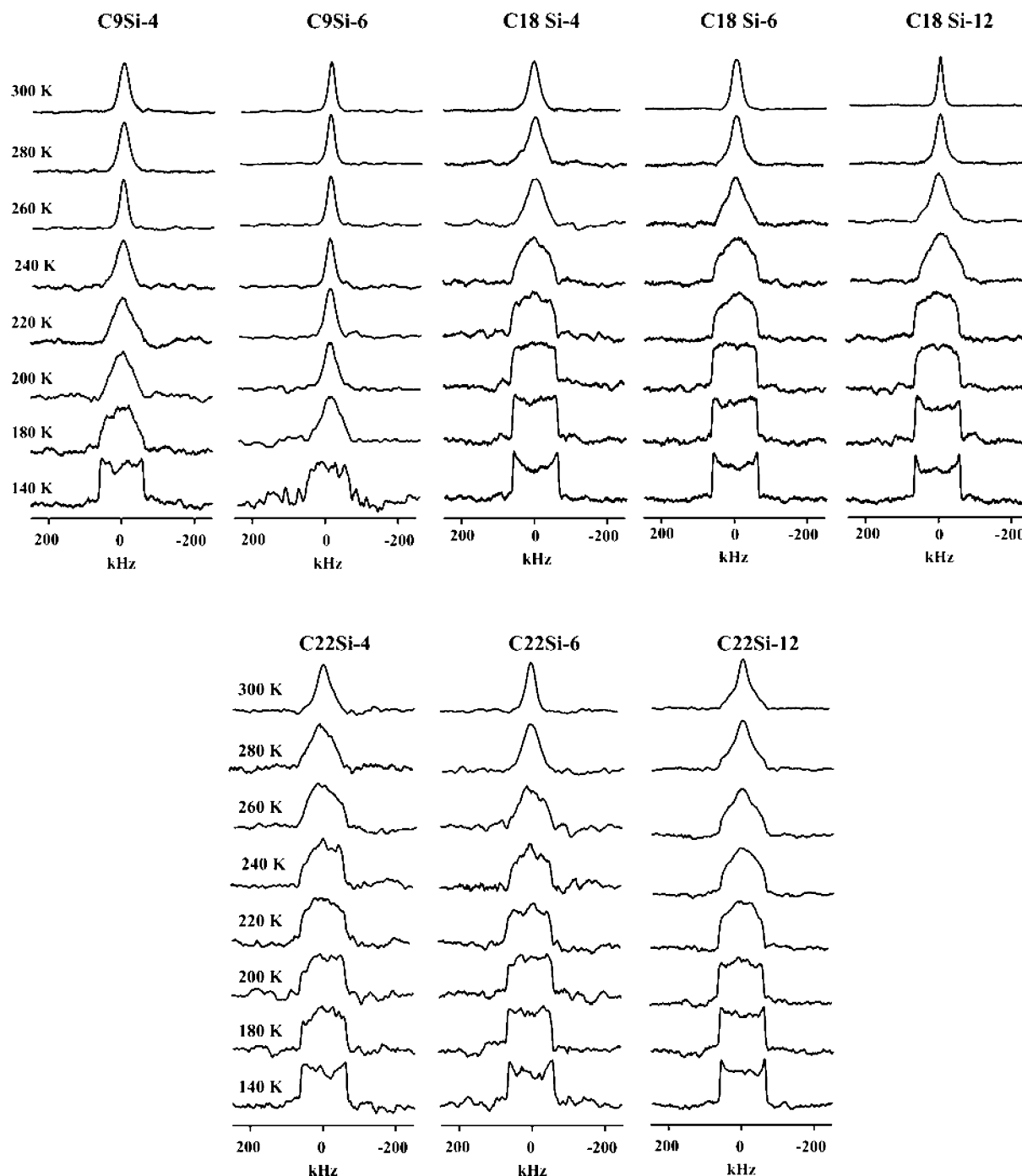
Figure 9. Variable temperature ^{2}H NMR line shapes for *n*-nonyl, *n*-octadecyl, and *n*-docosyl modified silica gels.

positions). In quite the same way for the silica gels with *n*-nonyl chains, larger fwhh's are observed for position C-4 than at position C-6. This observation—which is also supported by the fact that the decrease of the fwhh occurs at higher temperatures—can be attributed to a higher mobility of the untethered end of the *n*-alkyl chain.

^{2}H NMR Line Shape Analysis. The quantitative analysis of these experimental ^{2}H NMR line shapes involved the application of various motional models which were thought to be appropriate for the description of the motional characteristics of the present systems. In this context several motional models were examined which included both local and overall chain motions. Local chain motions were represented by trans−gauche isomerization while chain wobbling, restricted and unrestricted, and diffusive and jumplike chain rotation were used for the

description of overall chain motions. The primary goal of this part of the work was to find a motional approach that provides an adequately good fit for all systems studied here.

Of the various motional models examined here, the one where the *n*-alkyl chains are assumed to undergo a 32-site wobble (overall) motion, in combination with a two-site (local) trans−gauche isomerization process, was found to be the most appropriate for the reproduction of the variable temperature ^{2}H NMR line shapes of the present silica gels (see Experimental Section). Representative experimental ^{2}H NMR line shapes for the samples C9Si-4 and C18Si-12 along with their best fit theoretical counterparts are displayed in Figures 11 and 12, respectively. The variable simulation parameters are summarized in Tables 2−4, and further details are given in the Experimental Section. It should be noted that the line shape analysis was
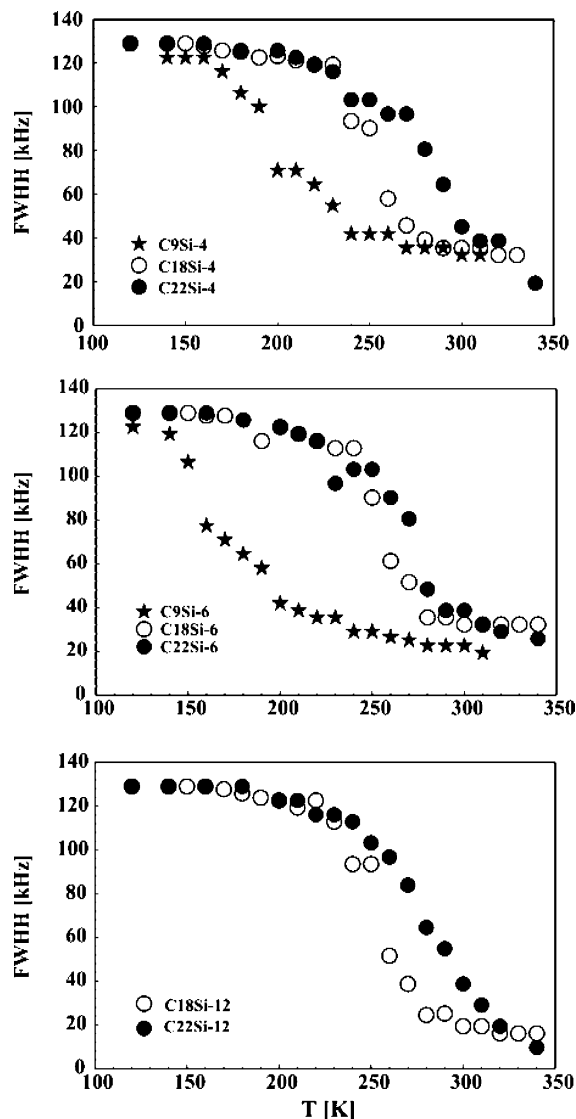
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Figure 10. Plots of full width at half-height (fwhh) of the broad spectral component in line shapes of *n*-nonyl, *n*-octadecyl, and *n*-docosyl modified silica gels vs temperature.

carried out by an independent fit for each system. Improvement and further refinement was achieved by cross-checking the parameters used for the various chain positions of the systems with identical chain length.

The derived motional correlation times clearly prove that the *n*-nonyl modified systems—in accordance with the conclusions from the fwhh values—possess the highest mobility. That is, for these systems both the overall wobble motion and the chain isomerization reach the fast motional regime at relatively low temperatures. For the other silica gels with longer *n*-alkyl chains (C18, C22), trans—gauche isomerization is found to set in first at lower temperatures, while overall chain wobbling becomes dominant at elevated temperatures.

In Figure 13 the correlation times of the overall wobble motions are given in an Arrhenius representation. It can be seen that the wobble rates are highest for the *n*-nonyl chains, while those for the *n*-octadecyl and *n*-docosyl chains are considerably smaller. The average activation energies for the chain wobble motion are found to be 22 ± 3, 47 ± 6, and 13 ± 2 kJ/mol for the *n*-docosyl chains, the *n*-octadecyl chains, and the *n*-nonyl chains, respectively. In general, the ^{2}H NMR line shapes are more sensitive to the (overall) wobble dynamics than to the (local) trans—gauche isomerization. The derived correlation
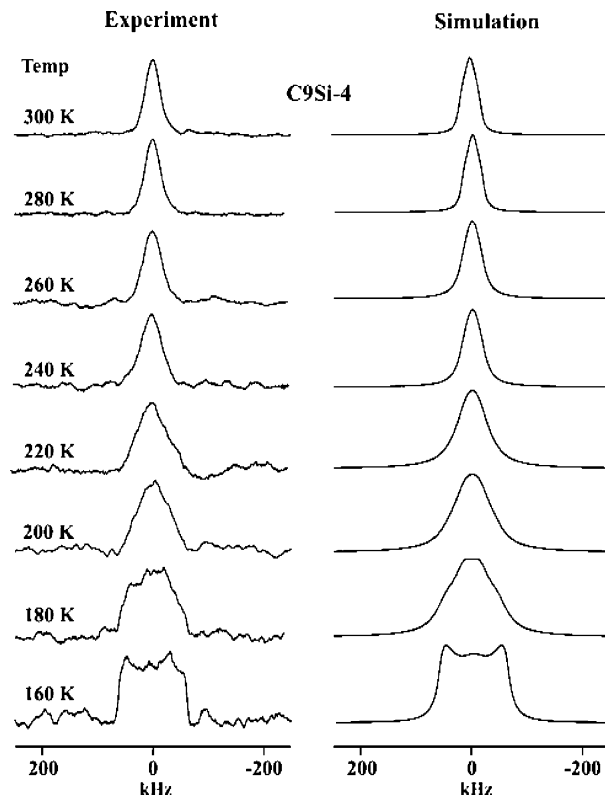

Figure 11. Experimental and theoretical ^{2}H NMR line shapes for C9Si-4 using 32-site wobble and 2-site trans—gauche isomerization with the rate constants and gauche percentages as given in Table 2.
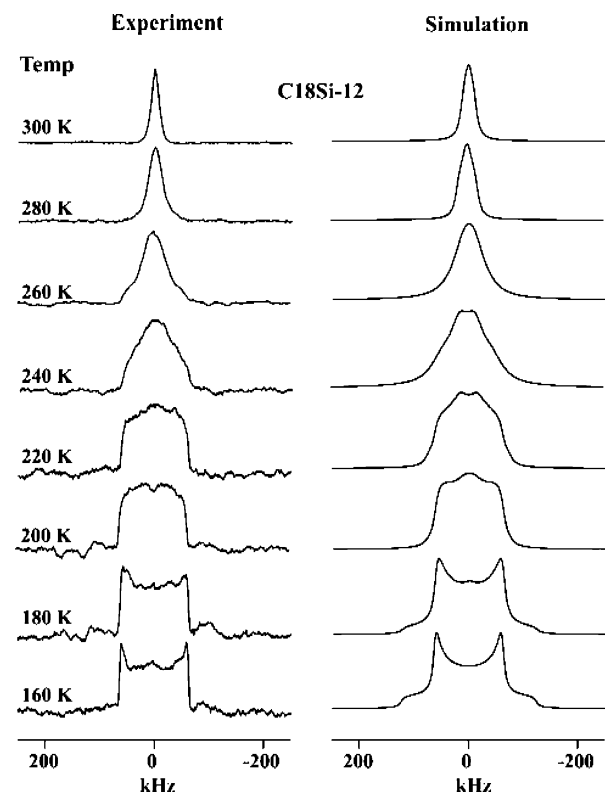

Figure 12. Experimental and theoretical ^{2}H NMR line shapes for C18Si-12 using 32-site wobble and 2-site trans—gauche isomerization with the rate constants and gauche percentages as given in Table 3.

times of trans—gauche isomerization therefore are characterized by a larger error, and a clear trend (i.e., temperature dependence) cannot be seen for these motional parameters (see Tables 2–4).
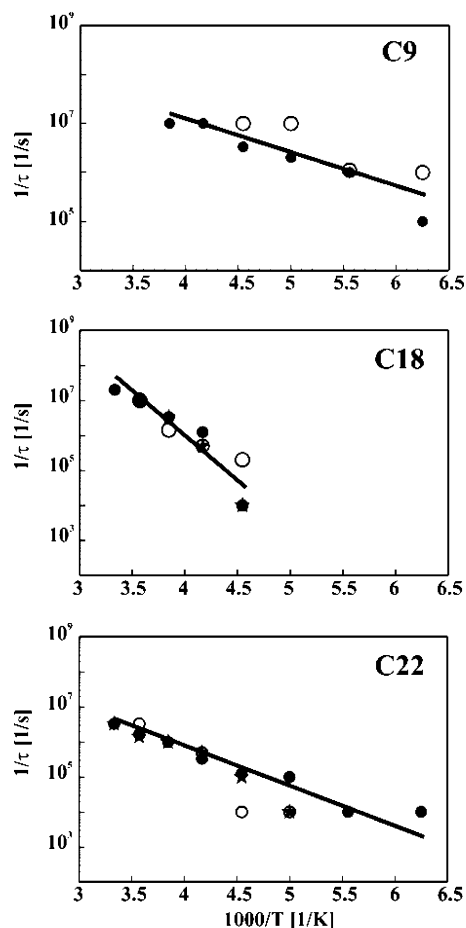
Figure 13. Arrhenius plots for the wobble motion of chains of various lengths in modified *n*-alkyl silica gels (data from deuterated position C-4 (●), C-6 (○), and C-12 (★)).

Figure 14. Proposed structures of C9 (left) modified silica gel at both low and high temperatures and C22 (right) modified silica gels at low temperature.

Consequently, no activation energies are given for this chain isomerization process.

Another ^{2}H NMR simulation parameter is the amount of gauche conformers (for results, see Tables 2−4), which according to model simulations mainly affects the width of the theoretical ^{2}H NMR line shapes. It should be noted that the present ^{2}H NMR line shape analysis was done completely independent from the former FT IR data analysis. Nevertheless, it is found that the derived values from both analyses are of the same order and exhibit the same tendencies: (i) shorter *n*-nonyl chains are conformationally less ordered, that is, possess a higher amount of gauche conformers, than the longer *n*-octadecyl and *n*-docosyl chains, and (ii) the conformational order decreases with increasing sample temperature. However, unlike the findings from the FT IR data analysis, a similar unusually high amount of gauche conformers at carbon position C-4 is not registered during the ^{2}H NMR data analysis.

Discussion

Conformational Order. The analysis of the various conformation-sensitive FT IR vibrational bands (CD$_2$ rocking, CH$_2$ and CD$_2$ stretching modes) has demonstrated that the conformational order is almost proportional to the actual chain length; that is, the shorter *n*-nonyl chains are conformationally more disordered than the long-chain analogues C18 and C22. For the latter chains, a quite distinct dependence of the conformational order on the actual chain position was observed at elevated temperatures. That is, the conformational disorder (and thus the conformational flexibility) is relatively high near the silica
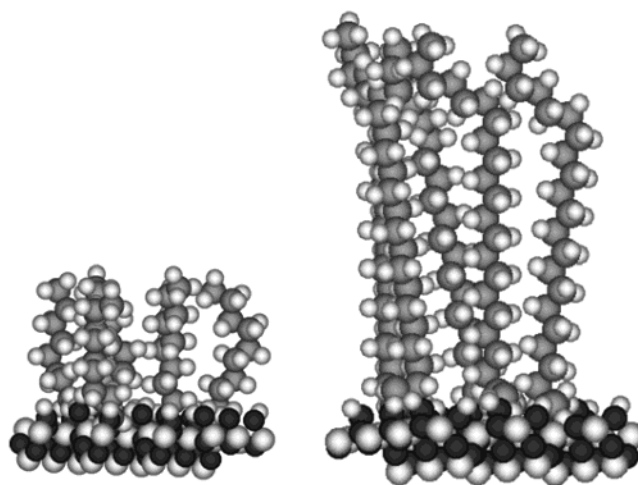
surface, decreases toward the center of the chain, and increases again near the chain end, which mainly can be attributed to a better chain packing in the inner section of the longer alkyl chains. With increasing temperature a "melting process" of the methylene segments sets in along with a decrease of the conformational order in the attached *n*-alkyl chains. The shorter *n*-nonyl chains do not exhibit such a position dependence of the conformational order. Moreover, the high gauche content in these shorter chains remains unaffected by the temperature. On the basis of these findings, a model of the *n*-alkyl chain structures in the present chemically modified silica gels has been developed which is schematically depicted in Figure 14.

It is expected that the surface coverage also has some effect on the conformational order of the present systems. The surface coverage can be directed by the synthetic route and the actual preparation conditions (amount of water, functionality of the silanes, etc.). For example, the SAM approach gives higher surface coverage than the surface polymerization method, which in turn yields higher ligand densities than the solution polymerization technique.[61] The closest spacing of *n*-alkyl chains is found in crystalline solids with a spacing restriction of 0.2 nm^2/ chains (8 μmol/m^2 for single layer of such molecules). This is also the approximate number of silanol groups present on the activated silica surface. The surface coverage typically ranges from 2 to 3.5 μmol/m^2 for monomeric phases and 3−6 μmol/ m^2 for polymeric phases. The present modified silica gels were prepared via solution polymerization using trifunctional silanes, leading to a relatively high surface coverage in the range 3.5− 6.2 μmol/m^2 (see Table 1). A closer look reveals that the surface loadings for *n*-nonyl and *n*-octadecyl samples are of similar order while the conformational order is much higher in the longer chains. Likewise, even though the surface loadings of the *n*-docosyl samples are higher than those of the *n*-octadecyl systems, a very similar conformational order is registered for both systems. Hence, it is the length of the *n*-alkyl chains rather than the surface loading that determines the conformational order of the present systems.

The present conformational data can be further compared with those from a recent study of SAMs on Au nanoparticles.[33,62] 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 analyzed in order to monitor the thermally induced onset of local disorder in the *n*-alkyl

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chains. From that work it was concluded that the conformational order is highest next to the Au surface and gradually decreases with the distance from the solid support. This is in contrast to the findings for the present systems with the same *n*-alkyl chain lengths, 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 the nature of the different solid supports (gold vs silica) and/or from different packing densities as a result of a different surface coverage (surface coverage data are not given in ref 33).

Maroncelli et al.[38] have investigated the conformational disorder in the high temperature crystal phases of long *n*-alkanes ($C_{21}H_{44}$ and $C_{29}H_{60}$) via CD_2 rocking vibrational modes. It was shown that the gauche conformers in these pure *n*-alkanes consisted entirely of kink conformations, distributed nonuniformly along the chain. The highest concentration was found at the chain ends, and the concentration at interior sites decreased exponentially on moving toward the center of the chain. In the case of *n*-docosyl silica gels, position C-12 in the inner part of the chain is in the trans conformation (0% gauche) at low temperatures ($T < 250$ K). The absolute amounts of gauche conformers at low temperatures are therefore comparable with that at position C-12 in crystalline $C_{21}H_{44}$. On the other hand, 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 $C_{21}H_{44}$ in the liquid phase.[39] Of course, 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. However, 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.

The analysis of CD_2 rocking bands is also well established in phospholipid membranes.[42-44] For the liquid crystalline phase of DPPC (1,2-dipalmitoyl-*sn*-glycero-3-phosphatidylcholine), it has been shown that the amount of gauche conformers is around 20% at positions C-4 and C-10, 10% at position C-12, but unusually high with 30% at position C-6.[42] For the present modified silica gels a somewhat different position dependence of the conformational order is registered. For instance, the C-6 and C-12 positions exhibit 15-20% gauche conformers even at the highest temperature (353 K) and thus have values more close to those found for positions C-4 and C-10 in the liquid crystal phase of DPPC. It should, however, be taken into account that the lengths of the alkyl moieties tethered to silica gels are somewhat longer than those in phospholipid membranes.

Information about the conformational status of an *n*-alkyl chain can also be obtained via the analysis of ^2H NMR line shapes. In fact, in the aforementioned work by Badia et al.,[33,62] ^2H NMR techniques were used to deduce the chain ordering in $C_{18}H_{37}SH$ derivatized gold nanoparticles on a qualitative level. According to this approach, the subsequent narrowing of the ^2H NMR signals originates from trans-gauche isomerization along with increasing gauche population in the *n*-alkyl chains upon temperature increase, in quite the same way as described in an earlier work on polymeric model membranes.[63] Thus, a single gauche bond—especially near the bound end of the *n*-alkyl chain—would cause a strong bend of the chain along with a pseudorotational motion of individual positions about the *n*-alkyl chain long axis. The resulting spectral narrowing can be expressed for example by the full width at half-height (fwhh). For the C_{18}/Au sample[33,62] bearing selectively deuterated *n*-alkyl

chains, the fwhh values were found to drop down in the vicinity of the calorimetric phase transition, suggesting that at this point the gauche population equals the trans population.[63]

For the present *n*-alkyl modified silica gels, the experimental fwhh values are given in Figure 10. A comparison of these curves with the derived amounts of gauche conformers from CD_2 rocking analysis reveals that for the present systems the changes of the fwhh with temperature as well as the plateau values cannot be explained simply on the basis of a change in conformational order. For instance, for C9Si-4 an almost constant gauche population was found, while the fwhh exhibits a characteristic temperature dependence. These differences can be understood by the fact that the above assumption holds only if the trans-gauche isomerization occurs in the fast motional limit and if this local motion is not superimposed by another motional contribution. In fact, as further discussed below, for the present silica gels, a second, overall motion has to be considered along with slow motional effects for both motional contributions. Thus, for the present systems, the fwhh mainly reflects the overall mobility of the *n*-alkyl chains; that is, a determination of the gauche population only on the basis of the derived fwhh is not possible.

However, from the ^2H NMR line shape simulations the amount of gauche conformers can be obtained without any restriction to the fast motional limit. A comparison of the derived amounts of gauche conformers from the ^2H NMR line shape simulations (see Tables 2-4) with those from the CD_2 rocking band analysis demonstrates that for chain positions C-6 and C-12 a reasonable agreement exists, while for chain position C-4 the derived data from the ^2H NMR analysis typically are about a factor of 2 lower than those from the FT IR data analysis.

Three reasons can be discussed for these discrepancies between the FT IR and ^2H NMR data. One explanation might be found in the lower quality (low signal/noise ratio) of the ^2H NMR line shapes. Another origin can be found in the fact that, unlike the case of the relatively simple curve fitting procedure for the CD_2 rocking band analysis, several simulation parameters have to be adjusted during the ^2H NMR line shape analysis. Both points give rise to a bigger error for the amount of gauche conformers during the NMR data analysis (20-30% as compared to 10-15% from the IR data analysis). A third reason could be found in the fact that the IR samples consist of KBr pellets with silica gels that are subject to a high external pressure during the pellet preparation, while the NMR samples are made without external pressure.

It is worthwhile to note that for the present chemically modified silica gels several authors distinguish between regions containing all-trans chains and regions with conformationally disordered chains containing gauche bonds.[9,10] This is mainly based on the observation of a low field shift of the ^{13}C NMR resonance of the inner methylene carbons, as is well-known for solid polyethylenes and solid *n*-alkanes.[64,65] In FT IR spectroscopy, such all-trans chains should also be visible via the formation of wagging band progressions[44] in the region between 1100 and 1350 cm^{-1}, as reported for pure hydrocarbons[38] in the crystalline and phospholipid membranes[66,67] in the gel state. The lack of these bands in the present silica gels suggests that the finite amount of gauche conformers (3-6% in the C18 and C22 modified systems) is sufficient to suppress the formation of progression bands.[66]

Chain Dynamics. On the basis of the derived fwhh values (from the experimental ^2H NMR spectra), it is quite obvious that the longer chains (C18, C22) on the silica surface are less mobile than the shorter chains (C9). The complex nature of the

samples and the characteristic spectral changes furthermore suggest that the *n*-alkyl chain dynamics cannot be described by a single motional contribution. For this reason several motional models were examined, such as two-site jumps, three-site jumps (rotation) combined with two-site trans−gauche isomerization, three-site trans−gauche isomerization combined with two-site chain wobbling, three-site trans−gauche isomerization combined with three-site jumps (rotation) and two-site wobble, and so forth. However, none of these models could provide a consistent reproduction of the experimental ²H NMR line shapes. Eventually, a combination of two motional contributions turned out to be most suitable for the theoretical description of the experimental ²H NMR line shapes of the present species. This motional approach considers a reorientational motion of the *n*-alkyl chains as a whole, modeled by a 32-site wobble process, along with a two-site trans−gauche isomerization process which accounts for the internal flexibility of the *n*-alkyl chain.

Additional support for the present motional approach is provided by the fact that for a given chain length the derived correlation times of the wobble process are almost independent of the particular chain position and are thus characteristic for the whole chain. Likewise, relatively high activation energies of 47 and 22 kJ/mol for the C18 and C22 chains were derived, which also point to a motional mode involving a larger molecular unit. In fact, these values are comparable to those reported for long-axis reorientation, for example, in liquid crystal polymers[68] or biomembranes.[69] For the shorter *n*-nonyl chains, lower activation energies for wobble motion are derived (13 kJ/mol), which can be understood by the smaller chain length, a reduced chain packing, and a lower chain order along with reduced spatial constraints for the overall motion in this system.

As already mentioned, for the local trans−gauche isomerization a similar pronounced temperature dependence is not observed. Nevertheless, it should be stated that this additional intramolecular motional contribution was absolutely necessary in order to reproduce the experimental ²H NMR line shapes. In addition, it can be seen that the derived correlation times for trans−gauche isomerization are of the same order as that discussed for solid polymers[59,68] or biomembranes in the gel phase.[69,70]

Quantitative studies on the *n*-alkyl chain dynamics in chemically modified silica gels are rare. A ²H NMR study on perdeuterated alkoxysiloxanes immobilized on a silica surface[11] showed motionally narrowed spectra at room temperature, irrespective of the chain length (C1 to C16). The motional averaging was far more noticeable in the longer chains than in the shorter ones. It was therefore concluded that the long chains (*n*-hexadecyl) are far from being fully extended, as, for example, in biological membranes.[54] Rather, they are expected to be randomly intertwined, similar to the amorphous region of a polymer, and an isotropic reorientation of the chain with a combination of torsional motions about the O−Si, O−C, and the various C−C bonds is discussed. This is in contrast to the results in the present work, where the shorter chains (C9) are found to be more mobile than the longer chains (C18 and C22). The most probable explanation for this discrepancy is given by the fact that in the former work[11] samples with perdeuterated chains have been examined. In this case the ²H NMR spectra are always a complex superposition of spectra from various chain segments, which, in general, is critical for a quantitative interpretation of the ²H NMR data. In addition, the surface loading might play a role which, in general, is lower (150−200 mg/g of silica) for the samples in that former work as compared to those of the present study (210−480 mg/g of silica).

Another comprehensive ²H NMR study has been performed previously on dimethyloctadecyl modified silica gels, which were deuterated either at position C-1 or simultaneously at carbon positions C-9 and C-10.[6] The authors have employed a 2-site jump motional model[47,63,69] (i.e., trans−gauche isomerization) of the *n*-alkyl chains for the description of the broad resonances observed in the low temperature spectra of these samples. The experimental ²H NMR line shapes at higher temperatures were analyzed by taking into account the heterogeneity of the samples.[71] Here, for the theoretical description of the ²H NMR line shapes, a superposition of two spectral components was assumed: (i) a broad (less mobile) component due to the aforementioned 2-site trans−gauche isomerization and (ii) a narrow (mobile) component based on a coupled rotational motion and trans−gauche isomerization (with identical correlation times) along with an inhomogeneous distribution of gauche conformers. On the basis of these model assumptions, the authors were able to reproduce the temperature and solvent effects on the ²H NMR line shapes of their samples. It turned out that−unlike the situation in our present work−the temperature effect can be mainly reproduced by changing the relative amount of the two motional components as well as the parameters for the distribution of gauche conformers. The thermal activation of the chain motions was almost negligible.

It is interesting to note that in the present work we were able to reproduce the experimental ²H NMR spectra over the whole temperature range solely on the basis of two superimposed motional contributions and without any superposition of two (or more) motional components, although the ²H NMR spectra are very similar to those reported in the work on the dimethyloctadecyl modified silica gels. The question therefore arises which motional model is more appropriate for the description of such chemically modified silica gels. The truth most probably lies somewhere in between.

Finally, it should be noted that the aforementioned dimethyloctadecyl modified silica gels were also examined by solid state ¹³C NMR line shape and spin−lattice relaxation.[7] It was demonstrated that the regions near the anchored end of the C18 chains (positions C-1 to C-3) are motionally more hindered, as compared to those near the unbound end near the C-18 position, which show very high mobility. The mobility of the region between carbon positions C-4 and C-15 was found to lie between these two extremes. Moreover, the experimental ¹³C spin−lattice relaxation data indicated a distribution of motional frequencies which was attributed to the inherent heterogeneity of the C18 modified silica gels. In our present work, the effect of the chain position on the mobility is not that evident. In this context, it would be interesting to examine for the present systems methylene segments that are farther apart from the silica surface but, however, are difficult to selectively deuterate.

Conclusion

In the present work, the conformational order of the silica gels chemically modified with selectively deuterated *n*-nonyl and *n*-docosyl chains has been investigated via ²H NMR and FT IR spectroscopy. Conformation-sensitive vibrational modes were analyzed over a large temperature range. It has been found that the conformational disorder in these systems is influenced by the sample temperature, the proximity of a particular segment to the silica surface, and the length of the *n*-alkyl chain. In general, a temperature increase induces conformational disorder in the *n*-alkyl segment. The conformational disorder in the shorter *n*-nonyl chains was found to be much higher than that in the longer ones (C18, C22).

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From an analysis of the ^{2}H NMR data, it has been shown that the *n*-alkyl chains undergo various molecular motions on different time scales. These motions include thermally activated 2-site trans−gauche isomerization and an overall wobble motion of the *n*-alkyl chains. The localized trans−gauche isomerization is generally faster than the overall chain motion, with the latter dominating the ^{2}H NMR spectra at higher temperatures. Moreover, the length of the *n*-alkyl chains attached to the silica surface plays an important role on the chain mobility. It has been observed that the shorter chains are more mobile than their longer counterparts in the immobilized state. In addition, it has been shown that the methylene segments farther apart from the silica surface exhibit a higher mobility than those nearer to the bound end. The derived activation energies for the wobble motion provided further support for the underlying motional model. In general, it could be demonstrated that for the present systems the increase in chain dynamics is accompanied by an increase in the conformational disorder.

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