Fourier Transform Infrared Spectrometric Determination of Alkyl Chain Conformation on Chemically Bonded **Reversed-Phase Liquid Chromatography Packings**

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A series of dimethyl-n-alkyl bonded phase sorbents ranging in length from C_1 to C_{22} have been prepared and studied by use of Fourier transform infrared spectrometry (FT-IR). Spectra have been produced for each of the bonded phases, and comparisons are made to the corresponding silane reagents. By use of assignments reported for nonplanar conformations of normal alkanes, the supramolecular structure of these bonded phase systems is examined. The presence of absorption bands at 1341, 1354, and 1367 cm⁻¹ in the bonded phase spectra confirms that bonded alkyl chains are bent, i.e., a significant fraction of the carbon-carbon bonds are in the "gauche" configuration. The degree of conformational disorder in chemically bonded stationary phases is shown to be comparable to that observed in the corresponding *n*-alkane liquids at room temperature and above. Phase transitions for the bonded phases are not observed at temperatures near or below the melting points of alkane and silane reagents of comparable length. Instead, the bonded phase chains are seen to retain a notable degree of disorder at low temperature. Finally, the effect of mobile phase environment on chain conformation is examined for a range of deuterated water/methanol mixtures varying from 70% to 100% methanol. Evidence is presented that in this range the mobile phase effects a significant increase in the order of the stationary phase.

The popularity of reversed-phase separations, particularly with C_{18} bonded packing materials, can be attributed to the success of this technique in solving a diverse array of problems. Surprisingly though, a detailed understanding of the mechanisms of solute retention is lacking. The difficulty in describing the retention process originates in the nature of the bonded phase itself. Almost all current types of bonded phases for use in liquid chromatography are produced from the reaction of chloro- or alkoxyalkylsilanes with silanol groups at the silica surface. In most instances, reaction conditions are such that a bonded monomeric layer results, with an overall density of chains of about half that of the corresponding liquids (1-3). As noted by Guiochon (4), the properties of bonded phases are thus expected to differ from bulk liquids, not only because the distance between chains is greater than in liquids but also because translational and rotational motions are absent.

The question of whether a bonded phase should be considered a surface or a thin liquid film has given rise to two theories of solute retention: adsorption and partitioning. Considerable effort has been expended by workers trying to

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classify retention as one of the two categories (5-7), but evidence for such a classification remains inconclusive. Clearly, before an accurate picture of solute retention can be built up, the microscopic properties of the anchored hydrocarbons must be elucidated. Little direct experimental data on the bonded phase structure exists, but a number of models have been advanced. Halasz and co-workers (8) originally pictured the bonded chains as "bristles" that extended vertically from the silica surface. A different structure has been proposed by Hemetsberger (9) who notes that "the nonpolar ligands of a chemically bonded phase are subject to the same solvophobic interactions as the solutes," and envisions the bonded ligands as folded to minimize exposed surface area. Lochmuller (5) has set forth an alternate arrangement in which groups of bonded chains associate to form pseudoliquid patches termed "liquid droplets". Gilpin has recently formulated a theory in which both folded and bristle states are possible and transitions between the two take place with changes in temperature or solvent (10, 11). More experimental data are obviously needed before any of these structural models can be seriously considered.

It is our belief that infrared spectrometry is an ideal technique for gaining insight into the structure of bonded alkyl phases. While characterization of LC microparticulates by infrared spectrometry has been attempted in previous studies (12-16), little information on the supramolecular structure of the alkyl surface has been obtained. In contrast, work on pure alkanes and model membranes has shown that IR spectrometry is quite useful in establishing the conformation of alkyl chains. Interpretations of the spectra are based upon normal coordinate calculations carried out by Snyder on chains in the all-trans conformation and in various "bent" conformations (17). This information has proven valuable in understanding solid-solid phase transitions in the n-alkanes (18-20) and in probing the role of chain disorder in the structure of model membranes (21-23).

The goal of this study was to use infrared spectrometry to elucidate the degree of conformational order of the alkyl chains of bonded phases. Spectra were made for a series of dimethyl-n-alkyl bonded phase sorbents with chain lengths ranging from C_1 to C_{22} , and comparisons were made to the corresponding silane reagents and in some cases to the parent alkanes. Further, the temperature dependence of C_{18} and C_{22} phases was studied, and the effect of mobile phase on chain conformation (for bonded phase materials) was examined.

EXPERIMENTAL SECTION

Chemicals. Dimethylchloroalkylsilane reagents were used to prepare the bonded phases. Trimethylchlorosilane, dimethyloctylchlorosilane, and dimethyloctadecylchlorosilane (ODS) were purchased from Petrarch Systems (Levittown, PA) and were used without further purification. Dimethylbutylchlorosilane, dimethyldodecylchlorosilane, and dimethyldocosylchlorosilane were synthesized from the corresponding terminal alkenes with dimethylchlorosilane. 1-Butene was obtained from Matheson Gas Products (East Rutherford, NJ), 1-dodecene from Aldrich

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Synthesis of Silanes. C_4 , C_{12} , and C_{22} silane reagents were synthesized by hydrosilylation by using the method of Berensen and de Galan (24). This reaction involves the catalytic addition of hydrosilane to the double bond of an alkene. By selection of dimethylchlorosilane and terminal alkenes, dimethylalkylchlorosilane reagents are produced. In the presence of hexachloroplatinic acid, the reaction is rapid and exothermic and addition to the double bond follows an anti-Markovnikov orientation.

Each of the silanes was purified by vacuum distillation three times. It should be noted that extreme care must be taken during distillation to allow the apparatus to cool before air is allowed into the system. It appears that in some instances (notably the C_{22} synthesis) the distillation temperature is above the autoignition temperature of the silane!

Bonded Phase Synthesis. A 4-fold excess of the silane reagent (based on 2 bonded groups/nm²) and an equal quantity of pyridene were added to 50 mL of dry toluene. A milky white precipitate formed at this stage which is believed to be a pyridinium chloride; only a small fraction of the silane reagent was observed to precipitate. Hot silica, dried for 8 h at 150 °C, was introduced into the reaction vessel and the slurry refluxed for 48 h. The bonded silica was subsequently washed with toluene, ether, methanol, 50% methanol/water, methanol, and finally, ether. The phases were stored after air-drying. Samples taken for carbon analyses were dried at 150 °C for 8 h. Carbon analyses were performed by Canadian Microanalytical Services (Vancouver, BC) or Gailbrath Laboratories (Knoxville, TN).

Spectrometry. The Fourier transform spectra were produced with an IBM Model IR 98 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and operated to give 2 cm⁻¹ resolution. A temperature accessory was constructed for the plate holders, consisting of coiled copper tubing and a Poly Science (Warrington, PA) temperature bath. With a dry ice/methanol slurry in the bath, cell temperatures as low as -30 °C were obtained. Upper temperatures of 47 °C were recorded with a heated water bath. Temperatures were measured with a chromel-alumel thermocouple and a Fluke Model 8084B digital voltmeter (Everett, WA). A dry air purge was utilized to help minimize interferences from water vapor and to prevent condensation at subambient temperatures.

Two types of IR plates and plate holders were used to obtain sample spectra. Conventional NaCl plates were used for the temperature studies, along with a holder of relatively large thermal mass. For solution spectra, a solution cell with Irtran-2 windows (Barnes Engineering, Stamford, CT) provided the required transparency and insolubility to water/methanol solutions. Bonded phase particulate samples were prepared simply by distributing the material evenly between two plates; no spacer was required. For solution spectra, dry particulates were placed between the Irtran-2 plates, the solution cell was assembled, and then solvent was carefully introduced. Silane reagents and alkane samples were run as thin films of variable thicknesses. A total of 200 scans were collected for the neat reagents, but bonded phase samples required 800-20 000 scans, depending on chain length and sample thickness.

RESULTS AND DISCUSSION

The measurement of infrared spectra of alkyl chains bound to microparticulates is plagued by two types of interferences: light scattering and background absorption. That light scattering is a serious interference is predictable; the mean diameter of HPLC microparticulates is 10 μ m while the spectral range in the mid-IR is about 2.5–20 μ m. Scattering is strongest at short wavelengths but decreases at long wavelengths. Further, the absorption spectrum of silica is strong and detailed. The combination of these interferences produces a background with a high overall optical density. Since bonded phases have loadings of 2–17% carbon, alkyl signals are small compared to the silica substrate. Thus, high quality spectra on bonded phases can only be obtained by



Figure 1. C_1 absorption spectra. A total of 20 000 scans were collected for the bonded phase spectra.



Figure 2. C_4 absorption spectra. The absence of 1354- and 1367- cm⁻¹ absorptions is predictable from the inability of four carbon chains to form kink and double-gauche conformers.



Figure 3. C_8 absorption spectra. The presence of nonplanar conformers is confirmed in the silane, and the conformers are probably present in the bonded phase sample.



Figure 4. C_{12} absorption spectra. A high proportion of kink conformations is apparent in the bonded phase spectrum.

averaging multiple scans and by careful background subtraction.

Examination of the absorption spectrum of the unmodified silica showed that two regions of the spectrum are relatively unobscured and yet correspond to areas of interest for normal alkanes: $3100-2700 \text{ cm}^{-1}$ and $1600-1320 \text{ cm}^{-1}$. The carbon-hydrogen stretching frequency for methyl and methylene groups is at $2850-2965 \text{ cm}^{-1}$ while carbon-hydrogen bending, scissoring, and wagging bands appear from 1470 to 1345 cm^{-1} . This paper shall concentrate exclusively upon these two spectral regions. Accordingly, FT-IR absorbance spectra for the two regions of interest were collected for each of the prepared bonded phases and the corresponding silane reagents



Figure 5. C₁₈ absorption spectra.



Figure 6. C22 absorption spectra.

in their liquid state (Figures 1–6). To facilitate comparison, the spectra have been normalized separately for each region. With the exception of the C_1 phase, an excellent correspondence exists for the bonded phases and silanes in each spectral region. Moreover, spectra are unique enough to permit identification of the C_1 , C_4 , C_8 , and C_{12} bonded phases by spectra alone; in contrast, the C_{18} and C_{22} phases are very nearly indistinguishable. In the C_1 bonded phase spectrum, we are as yet unable to assign the absorbance signal at 2851 cm⁻¹.

Spectral assignments are based on Snyder's calculations on model *n*-alkanes (17-19). Figure 7A illustrates the zigzag, planar, or "all-trans" conformation for n-octadecane. This conformation predominates in the lowest temperature crystalline forms of long chain *n*-alkanes. The infrared spectra of such solids notably lack absorption bands at 1367, 1354, and 1341 cm⁻¹. Snyder has assigned these to methylene wagging vibrations localized on short sequences of bonds having specific conformations. The absorption band at 1341 cm⁻¹ originates from molecules which have the "end-gauche" conformation, as illustrated in Figure 7B for octadecane. In this conformation, the penultimate bond is in the gauche state (g or g' depending upon the sign of the rotation), and one or more adjacent bonds are in the trans configuration. We use the symbolism $gt_m, m \ge 1$, where m is the minimum number of trans bonds in the chain adjacent to the defect so that the frequency of the transition is chain length independent. The absorption band at 1354 cm⁻¹ indicates a conformer with two consecutive gauche bonds $(t_m ggt_m, m, m^* \ge 0)$ as shown in Figure 7C for octadecane. This "double-gauche" conformer is prominent in the liquid-state spectra of *n*-alkanes and represents a severe departure from planarity. The absorption band at 1367 cm⁻¹ arises from wagging motions localized at a gauche-trans-gauche' sequence of rotations $(t_m gtg't_m, m, m^*)$ ≥ 0), or to a gauche-trans-gauche sequence (t_mgtgt_m, m,m) ≥ 0). The former conformation shown in Figure 7D connects parallel but laterally displaced planar segments and is commonly called a "kink". The later conformation (not shown) represents a significant departure from linearity.

The presence of nonplanar conformations is clearly indicated in the C_4 , C_8 , C_{12} , C_{18} , and C_{22} bonded phase spectra (Figures 2–6) which exhibit absorbance bands in the 1367– 1341-cm⁻¹ region. Moreover, comparison of the relative in-



Figure 7. Alkyl chain conformations. The nonplanar conformations shown give rise to localized mode vibrations which are observed in the infrared spectrum: (A) all trans; (B) end-gauche, 1341 cm^{-1} ; (C) gauche-gauche (or double-gauche), 1354 cm^{-1} ; (D) kink, 1367 cm^{-1} .

tensities of the nonplanar absorption bands for the bonded phases with the corresponding liquid phase silanes indicates the bonded phases have a degree of disorder comparable to that of a liquid. It is interesting to note that only the endgauche absorption (1341 cm⁻¹) is observed in the spectra of the C₄ bonded phase and silane. This is because the kink (1367 cm⁻¹) and double-gauche (1354 cm⁻¹) conformations are not possible for the four carbon chain.

Because the spectra region $1367-1341 \text{ cm}^{-1}$ seemed to give the most information about the supramolecular structure of the *n*-alkane bonded reversed-phase materials, a series of studies of this region were undertaken for several types of octadecyl samples, including bonded silicas, silicas physically coated with octadecane, pure octadecane in microcrystalline form, and its corresponding silane, ODS. The coated C₁₈ phase was prepared by addition of silica to a solution of octadecane in carbon tetrachloride, followed by slow evaporation of the solvent with continuous stirring. The phase so produced was 9.06% carbon by weight.

Figure 8 shows absorption spectra for the four octadecyl cases at 44 °C. This temperature is well above the melting point for octadecane and ODS, so the spectra of these are from the liquid state. Comparison of the spectra immediately reveals a high degree of similarity. It is clear that in all cases there are substantial numbers of chains which contain gauche bonds, as can be judged from the presence of absorption bands at 1367, 1354, and 1341 cm⁻¹, shown in more detail in Figure 9. In fact, it is possible to give a semiquantitative interpretation of the spectra in terms of the number and types of gauche defects. Two assumptions are necessary: the first is that one can use the rotational isometric state model (25) to predict the distribution of gauche defects for the liquid C_{18} alkane, and the second is that the extinction coefficients for the absorption bands do not vary appreciably between the four cases examined. Thus, the normalized intensity ratios from C_{18} liquid bands to the other materials can be used to estimate the concentration of conformational defects for each sample.

Application of the rotational isomeric state model (25, 26) to the C_{18} alkane at 44 °C, assuming an effective gauche-trans



Figure 8. C₁₈ temperature study, 44 °C. The absorption at 1409 cm⁻¹ in the silane and bonded phase is thought to be due to a methyl bending vibration for CH₃ attached directly to silicon. All spectra exhibit signals at 1341, 1354, and 1367 cm⁻¹.



Figure 9. Enlargement of Figure 8 showing conformational detail. Assignments are as follows: u, CH₃ symmetric deformation (umbrella mode); gtg', kink conformation; gg, gauche-gauche conformation; gt, end-gauche conformation.

energy difference of 500 cal/mol and a gg' energy of 3000 cal/mol, yields the following estimates for the numbers and types of defects. First, we calculate that 42% of the end methyl groups will be in the end-gauche configuration. Second, an average of 5.4 of the internal C-C bonds per chain will be in the gauche configuration. Third, an average of 1.3

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pairs of bonds per chain will be in the double-gauche (gg) configuration. Fourth, an average of 1.4 triple sequences per chain will be of the type gtg' (kink) or gtg. This theoretically derived picture of the C_{18} *n*-alkane in the liquid state as a highly disordered entity is quite consistent with a large body of experimental data (27). In order to estimate the number of defects per chain in the other materials, the spectra have been normalized to a "standard" band. For this purpose, the methylene scissoring mode at 1470 cm⁻¹ has been selected.

In a comparison of the liquid silane with the liquid alkane, if the end effect of the silane group can be ignored, the rotational isomeric state model would predict both alkane chains to have identical numbers and types of gauche defects. Indeed, reference to Figure 9 shows the intensities of the 1367-cm⁻¹ (gtg, gtg') and 1354-cm⁻¹ (gg) bands to have nearly identical intensities in both cases. The 1341-cm⁻¹ bands are probably not strictly comparable because of the presence of an overlapping band in the silane spectrum originating from the methyl silane groups, as in Figure 1. It is comforting to note that for the silane, the intensity of the methyl umbrella mode at 1379 cm⁻¹ is half that of the alkane, exactly as expected, since the silane has only one methyl group.

Comparison of the coated and bonded phases with the pure liquids reveals a considerable reduction in the number of defects per chain. For the kink states, it amounts to a factor of 0.8 for the bonded phase and 0.3 for the coated, while for the double-gauche defects it amounts to 0.5 for the bonded phase and 0.4 for the coated. In the case of the coated phase, we estimate that the number of end-gauche defects is decreased by a factor of 3 as well. These results can be explained in terms of the steric restrictions imposed by the neighboring chains (28). Clearly, gg configurations would severely disrupt the lattice of the bonded and coated phases and therefore would not be energetically favored. Also, it seems reasonable to assume that, for the phases, most of the absorption at 1367 cm^{-1} arises from the gtg' (kink) states rather than the gtg states, because the kinks are undoubtedly more easily incorporated into the lattice (29). It should be emphasized that although the alkane surfaces of the coated and bonded materials are more ordered than the corresponding liquids, they still contain several gauche bonds per chain.

Figure 10 shows absorption spectra for the same four cases at 10 °C. Both the alkane and silane are crystalline solids at this temperature. As expected, their spectra are considerably sharper, and the absorption bands corresponding to conformational defects are markedly decreased. An expanded display of the region 1400-1320 cm⁻¹ is presented in Figure 11 to facilitate comparison. The 1368-cm⁻¹ transition seen in the alkane is assigned to the methyl umbrella mode rather than a kink mode. The former is known to shift as much as 10 cm^{-1} to lower energy upon crystallization (20). Furthermore, it is noted that for the alkane, the gg defects are virtually absent while the end-gauche defects are decreased by a factor of approximately 4. Similarly, in the case of the silane, the gg configurations have disappeared and the end-gauche and kink configurations have decreased by over a factor of 3. In contrast, the spectra of the bonded and coated phase materials are virtually unchanged with the decreased temperature. This result is consistent with the idea that in the absence of a phase transition, the population of the various rotational isomers is not strongly temperature dependent in this temperature region. At -30 °C (Figures 12 and 13) all of the samples exhibit chain ordering. The 1354-cm⁻¹ (gg) and 1341-cm⁻¹ (gt) bands are completely absent for octadecane and octadecane-coated silica samples. The silane and bonded silica no longer show absorption bands at 1354 cm⁻¹. The spectra for C_{18} coated phase and ODS bonded phase are similar in that, even at low temperatures, both phases exhibit signs of chain



Figure 10. C_{18} temperature study, 10 °C. The neat C_{18} sliane and alkane show signs of ordering, while the bonded and coated spectra are relatively unchanged from 44 °C.





Figure 12. C_{18} temperature study, -30 °C. All spectra show signs of ordering. The bonded phase spectrum still exhibits evidence of end-gauche conformations.



Figure 13. Enlargement of Figure 12 showing conformational detail.

Figure 11. Enlargement of Figure 10 showing conformational detail.

disorder in the form of kinks. The peak splitting observed for the pure C_{18} and ODS samples at -30 °C arises from factor group splitting, which requires two conditions: inequivalence in the unit cell and concerted interactions among vibrational motions (30). Factor group splitting is not expected in an irregular lattice.

A second temperature study was made on a C_{22} bonded phase and the corresponding C_{22} silane. Spectra were recorded at four temperatures, ranging from +47 to -30 °C (Figures 14–17). Spectral trends are similar to those recorded for the C_{18} silane and bonded phase samples. Again, factor group splitting is not observed or expected in the C_{22} bonded phase spectra (Figure 14) but is prominent in the silane spectra (Figure 16). In Figure 15 it is clearly seen that the bonded phase absorption at 1354 cm⁻¹ (double-gauche conformer) decreases strongly with temperature; at -30 °C, no absorption is detectable. Kink conformations are also seen to decrease.

 C_{22} silane spectra are shown in Figures 16 and 17. Unlike the bonded phase spectra, changes in the absorption bands are discontinuous and indicate a phase transition in the vi-



Figure 14. $\rm C_{22}$ bonded phase temperature study. Ordering is apparent with decreasing temperature.





Figure 16. C_{22} silane temperature study. Evidence for a phase transition is apparent in the region of 32 °C. The actual melting point of dimethyldocosylchlorosilane is 38 °C.



Figure 15. Enlargement of the conformational detail of Figure 14. The 1341-cm⁻¹ absorption denoting double-gauche conformations decreases to zero at -30 °C. Decreases are also observed in the 1367-cm⁻¹ transition (kink conformation). The number of end-gauche conformations remains relatively constant over the specified temperature range.

cinity of 32 °C. The actual melting point of the silane was measured at 38 °C. Examination of the enlarged 1400–1320-cm⁻¹ region also indicates a considerable ordering of the silane chains. Kink and double-gauche conformations are less

Figure 17. Enlargement of the conformational detail of Figure 16. Both double gauche and kink transitions (1354 and 1367 cm^{-1}) are decreased with decreasing temperature.

intense at lower temperatures but are still present. It is interesting to note that at 47 °C, the C₂₂ silane has approximately 30% more kink defects and approximately twice as many gg defects as the C₂₂ bonded phase.

A final experiment was designed to probe mobile phase effects on alkyl bonded packings. The mobile phase presents



Figure 18. Methanol/deuterated methanol comparison spectra. The dashed lines denote the spectral regions of interest in the bonded phase studies.

an added complication in IR spectrometry. All solvents of chromatographic interest contain carbon-hydrogen bonds. As a result, they exhibit intense absorption peaks in the same regions as the alkyl bonded phases. However, by using completely deuterated solvents, the overlapping solvent peaks can be shifted to lower energies where they no longer interfere (Figure 18).

A series of spectra were obtained for the C_{18} bonded silica in the presence of deuterated methanol-deuterium oxide solutions of varying compositions (Figure 19) and the 1400– 1320-cm⁻¹ region is presented for close inspection. When the data are normalized to the intensity of the methylene scissoring band at 1470 cm⁻¹ and compared with the data on dry packings, it becomes apparent that the number of gtg' and gt defects per chain are decreased by a factor of 2 while the gg defects are decreased by almost a factor of 3. This marked degree of chain straightening is attributed to the selective adsorption of organic modifier (methanol) into the mobile phase (31–34). It is interesting to note that over the range of compositions studied, there are no measurable changes in conformations of the chains.

The data obtained in this paper, together with studies of related model systems, allow the construction of a detailed description of the supramolecular structure of the long-chain bonded alkyl phases. In the dry materials, significant absorption intensities are present at 1367, 1354, and 1341 cm⁻¹. These bands have been shown by Snyder to arise from methylene wagging vibrations on sequences of bonds involving gauche configurations (17). Because it is known from theory (25, 26) and experiment (27) that nearly 40% of the internal carbon-carbon bonds are in the gauche configuration in long-chain liquid *n*-alkanes at room temperature, it seems reasonable to conclude that the dry C_{18} bonded phases are quite disordered. However, this does not imply that the alkane phase should be considered as a thin liquid film. First of all, two types of motion which characterize a liquid are absent, namely, translational diffusion and rotational Brownian



Figure 19. C₁₈ bonded phase solution spectra. The bonded phase sorbent was slurried in deuterated methanol/deuterium oxide solutions. Mixtures below 70% methanol- d_4 were not feasible because of wettability limitations of the bonded phases. The spectra of bonded phase sorbents in the presence of mobile phase are similar to the dry phase. Kinks and end-gauche conformations appear to be less favored in the presence of the mobile phase (see also Figure 9), while double-gauche conformations are greatly decreased.

motion. Clearly, there will be a net orientational order in the system. Second, the presence of nearby chains at fixed distances will influence the relative numbers of various conformational defects of the chains (28). Also, it can be argued that the degree of order of the chain probably increases considerably near the silica surface. This is because gauche bonds formed low on the chain will cause a more severe overall bending of the chain than gauche bonds near the top of the chain. In the case of model membranes, such notions have been verified both theoretically (35) and experimentally (36). Third, it must be pointed out that infrared spectrometry does not directly give dynamical information about chain motion, because the time scale for the absorption event is approximately 10^{-15} s. Thus a "glasslike" state is indistinguishable from a "liquidlike" state.

The influence of mobile phase environment in increasing the ordering of the alkyl chains can be attributed to binding of the organic modifier to the reversed phase. It seems reasonable that the methanol molecules could behave like a surfactant, orienting themselves so that the hydrophobic methyl groups intercalate between the chains and the polar hydroxy groups project into the bulk mobile phase. Thus, the hydroxyls would be available for hydrogen bonding to nonintercalated methanols. This packing of mobile phase molecules between the alkyl chains would favor considerably more ordered (straightened) alkyl conformations, as observed. The apparent ordering is consistent with Gilpin's dual state model for bonded phases (10, 11). Thus, a disordered "folded" state is favored when the packing is either dry or in the presence of a nonwetting mobile phase, and a more ordered "bristle" state is favored when the chains are wet with a mobile phase of high organic content. However, in this bristle state, there is still on average at least one gauche defect per chain.

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Determination of Nitrogen Dioxide by Pulsed Thermal Lens Spectrophotometry

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A thermal lens spectrophotometric system, consisting of a pulsed dye laser source, a photomultiplier, and a wave memory controlled by a microcomputer, is used for a determination of atmospheric NO2. The enhancement factor for the sample In various media is calculated by using the theoretical equation and the optical parameters and compared with the observed value for the gaseous and liquid phase samples. The agreement of the observed value with the theoretical value was fair. For a laser pulse energy of 1 mJ, a signal enhancement of 10³ is expected in comparison with a conventional spectrophotometer. The determination of NO₂ is carried out by using a dye laser with a pulse energy of 20-40 μ J, and a detection limit of 0.8 ppm was achieved. Verification of the theoretical equation and advantages of a pulsed laser source for the determination of the gaseous sample are discussed in comparison with a CW laser excitation method.

Nitrogen oxides, especially in the form of NO_2 , are very important in air pollution, since the interaction of NO_2 in the atmosphere with sunlight and unsaturated hydrocarbons produces hazardous photochemical oxidants. Therefore, a sensitive and reliable means for trace analysis of NO₂ is required. Several analytical methods are currently proposed, and some instruments such as a chemiluminescent NO₂ monitor are used in practical applications (1). However, the fingerprinting assignment by a spectrometric method is essentially impossible for the determination of NO₂. Many laser spectrometric methods are proposed to overcome this problem. Laser fluorimetry using Ar⁺ and He-Cd lasers has been investigated, and its analytical detection limits are reported to be 1-3 ppb and 0.6 ppb, respectively (2-4). A fluorimeter with a tunable dye laser and a fluorescence monochromator may have a potential for the fingerprinting determination of NO₂. The use of the fluorescence monochromator enables normalization of the fluorescence intensity of NO₂ with the Raman bands of nitrogen and oxygen in the atmosphere (5). The detection limit is reported to be 600 ppb for the direct determination and 20 ppb for the trap method. Barnes et al. applied a tunable dye laser to the measurement of the excitation spectrum of NO_2 in flames (6). The detection sensitivity in that study was on the order of 200 ppm.

Spectrophotometry is one of the most reliable methods, but a main disadvantage may be its poor sensitivity. In order to remove this limitation, a few laser spectrophotometric methods have been investigated. Latz et al. have proposed the idea of using intracavity quenching of laser emission (7), and Atkinson et al. have obtained a linear analytical curve in the 5-100 mtorr range of NO_2 (8). Angus et al. have used photoacoustic spectrometry for the detection of atmospheric NO₂ (9). Using a continuous wave (CW) rhodamine 6G dye laser with an output power of 250 mW, they have obtained the detection limit of around 20 ppb. Claspy et al. have used a flashlamp-pumped pulsed dye laser with an output energy of 7 mJ/pulse (average power, 210 mW) and demonstrated the detection of 2 ppm NO_2 in air at 10 torr total pressure with a S/N ratio of 100 at an average power of 100 mW (10). The