TABLE V: Selected Transition Probabilities for O₂ + Cl₂ at Two **Total Energies**

			Povsa		
E, eV	transition	P _{exact} ^a	$\bar{n}_2 = n_2$	$\bar{n}_2 = n_{2a}$	$\bar{n}_2 = n_2'$
0.5	00 → 00	0.739+0	0.361-1	Ь	
	$00 \rightarrow 01$	0.242+0	0.120+0	0.148+0	0.182+0
	$00 \rightarrow 02$	0.187-1	0.199+0	0.245+0	0.270 ± 0
	$00 \rightarrow 03$	0.323-3	0.220+0	0.208+0	0.118+0
2.0	$00 \rightarrow 00$	0.171-4	0.303-7		
	00 → 01	0.243-3	0.512-6	0.708-6	0.977-6
	$00 \rightarrow 02$	0.167-2	0.433-5	0.794–5	0.145-4
	$00 \rightarrow 03$	0.720-2	0.244-4	0.571-4	0.131-3

^aReference 7. ^bAll \bar{n}_2 choices give the same result.

ceptable results, the TVSA gives unacceptable results, and while some trends seen in the atom-diatom case are also seen here, new trends are seen due to the possibility of exciting more than one vibrational mode. A starting point for a discussion of the first three items is based upon the analysis of sudden approximations by Chang, Eno, and Rabitz.⁵ These workers have based their analysis upon a dedimensionalized Schrödinger equation for two colliding, rotating, and vibrating diatomic molecules which yields several criteria for energy suddenness. As a consequence, these workers have predicted that the TVSA would not give reliable results. The question was how poorly would the TVSA results agree with the exact results? The comparisons provided in the current paper clearly demonstrate the answer to this question is the TVSA does not work at all. The systems studied here under the TVSA do not even exhibit the usual trends seen in sudden approximations such as an improvement as the total energy increases.

The poor performance of the OVSA for $O_2 + Cl_2$ and the good performance of the OVSA for $H_2 + Cl_2$ might have been expected on the basis of an analysis similar to that of ref 5. Referring to eq 1, one sees that $m_{\rm Cl} \gg 3m_{\rm O}$, whereas, $m_{\rm Cl} \gg 3m_{\rm H}$. The question was how different do the masses need to be? Apparently a factor of 10–11 in this inequality allows sudden behavior to take place; therefore, some boundaries have been established, but further work involves finding how small the mass ratio can be and still give acceptable answers.

A final interesting feature is that the average % errors in the OVSA transition probabilities for all probabilities reported here in the range 0.1-1.0, 0.01-0.1, and 0.001-0.01 are 7, 30, and 50, respectively. Clearly the OVSA performs substantially better for larger transition probabilities. These comments hold provided the OVSA is justified; the $O_2 + Cl_2$ system does not exhibit this behavior.

In closing, the following conclusions are drawn. The OVSA is capable of good to excellent results, even for large Δn_2 and Δn_1 , for $m_A/m_B \leq 35$ (for a collision between the homonuclear diatomic molecules A_2 and B_2 , with B_2 treated in the VSA) and for probabilities down to 0.1. Further, the OVSA is useful qualitatively for even smaller probabilities. Out of the choices, n_2 , n_2' , and $n_{2a} = (n_2 + n_2')/2$, for \bar{n}_2 , n_2' , or n_{2a} give the most accurate probabilities. The maximum value of n_1 required for converged answers in the fully coupled exact solution is also the largest n_1 which needs to be included in the partially coupled OVSA solution. The OVSA calculations are ~ 30 times faster than the exact calculations. The TVSA does not give acceptable probabilities for the $H_2 + Cl_2$ and $O_2 + Cl_2$ systems.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. Partial support for this work also came from the University of Nebraska at Omaha Committee on Research. We also thank the University of Nebraska at Omaha Departments of Chemistry and Computing Center in general and the reviewers for helpful comments.

Registry No. H₂, 1333-74-0; O₂, 7782-44-7; Cl₂, 7782-50-5.

Deuterium Nuclear Magnetic Resonance Studies of Alkyl Modified Silica

M. Gangoda,[†] R. K. Gilpin,^{*,†} and J. Figueirinhas[‡]

Departments of Chemistry and Physics, Kent State University, Kent, Ohio 44242 (Received: November 18, 1987; In Final Form: January 23, 1989)

Selectively deuterated n-alkyldimethylchlorosilanes were synthesized and used to prepare both chemically modified and physically coated porous silica. ²H NMR spectra were recorded on these modified solids at 46.1 MHz. A sharp liquidlike resonance was observed for the physically coated sample indicative of a complete averaging of the quadrupole interactions. Broad Lorentzian-shaped resonances were observed from all of the chemically modified surfaces with widths less than that expected for rigid-limit conditions. Similar line widths were observed for deuterons in the first and fourth positions and decreases in widths for deuterons toward the free end of the chain. The line shapes are ascribable to the presence of slow motions and the absence of a unique axis of reorientation. Spin-lattice relaxation times also were measured as a function of temperature for the chemically modified surfaces. These latter data as well as line width data indicate that there are at least two different motional domains.

Introduction

Alkyl modified silicas are used widely as stationary phases in liquid chromatography (LC). Often these materials are prepared from the corresponding chlorosilanes and used in the reversedphase mode with polar mobile phases such as binary combinations of water and methanol or water and acetonitrile. Since alkyl modified silicas are such an important class of LC surfaces, they have been studied extensively via a variety of chromatographic and spectrometric methods. In the latter case, infrared,¹⁻³ electron spin resonance,⁴ nuclear magnetic resonance,⁵⁻¹³ and neutron

^{*} To whom correspondence should be addressed. [†] Department of Chemistry.

¹Department of Physics.

⁽¹⁾ Sander, L. C.; Callis, J. B.; Field, L. R. Anal. Chem. 1983, 55, 1068.

 ⁽²⁾ Suffolk, B. R.; Gilpin, R. K. Anal. Chem. 1985, 57, 596.
 (3) Suffolk, B. R.; Gilpin, R. K. Anal. Chem. Acta 1986, 181, 259.

⁽⁴⁾ Gilpin, R. K.; Kasturi, A.; Gelerinter, E. Anal. Chem. 1987, 59, 1177.

⁽⁴⁾ Glipin, R. K.; Kastun, A.; Gelerinter, E. Anal. Chem. 1967, 39, 1171.
(5) Gangoda, M. E.; Gilpin, R. K. J. Magn. Reson. 1983, 53, 140.
(6) Sindorf, D. W.; Maciel, G. E. J. Am. Chem. Soc. 1983, 105, 1848.
(7) Sindorf, D. W.; Maciel, G. E. J. Phys. Chem. 1982, 86, 5208.
(8) Gilpin, R. K.; Gangoda, M. E. J. Magn. Reson. 1985, 64, 408.
(9) Sindorf, D. W.; Maceil, G. E. J. Am. Chem. Soc. 1983, 105, 3767.
(10) Gilpin, R. K.; Gangoda, M. E. J. Chromatogr. Sci. 1983, 21, 352.
(11) Albert, K.; Evers, B.; Bayer, E. J. Magn. Reson. 1985, 62, 428.



Figure 1. Uniaxial rigid-limit powder spectrum simulated using a quadrupole coupling constant of 165 kHz and a natural line width of 0.25 kHz: (a) ${}^{3}/{}_{4}Q_{0}$, (b) ${}^{3}/{}_{2}Q_{0}$.

scattering¹⁴ techniques have been utilized to investigate topics ranging from elucidation of the bonding chemistry and surface homogeneity of the bound layers to characterization of the conformational and motional dynamics of the attached groups.

Chromatographic surfaces have been examined by both solidstate^{6,7,9} and conventional solution NMR^{5,10-13} techniques. In the latter case, selective ¹³C labeling was used to enhance sensitivity and to minimize interferences from overlapping resonances. 5,10,12,13 The terminally labeled methyl groups are useful surface-bound probes for investigating various interfacial properties because of the rapid reorientation of the methyl group due to internal free rotation and chain segmental motion.^{6,12} A number of properties of surface immobilized groups have been investigated by using the technique. Differences in line shape and spin-lattice relaxation time have been correlated with alkyl chain length, position of labeling, bonding chemistry, and properties of the contact solvent. 8,10,12,13

Although ²H NMR has been used extensively to investigate the dynamic nature of restricted or semirigid systems such as membranes,¹⁵⁻¹⁸ liquid crystals,^{19,20} and macromolecules,^{21,22} the application of this technique to study chemically modified silica has been limited.^{23,24} In the present investigation, selectively deuterated n-alkyldimethylchlorosilanes were synthesized and used to prepare chemically and physically altered porous silica. Wide-line NMR spectra and spin-lattice relaxation times were acquired on these modified materials as a function of temperature.

The relevant ²H NMR theory to describe motional and conformational aspects of bonded chains is similar to that applied to polymer, liquid crystal, and lipid bilayer systems.²⁵⁻²⁷ In the absence of motion (i.e., the rigid limit) a carbon bound deuterium atom with the C⁻²H bond oriented at an angle θ with respect to external magnetic field gives rise to a doublet with a quadrupole splitting $\Delta \nu$:²⁸

$$\Delta \nu = \frac{3}{4}Q_0(3\cos^2\theta - 1)$$
 (1)

where Q_0 is the static quadrupole coupling constant. For a

- (15) Brown, M. F.; Seelig, J.; Haberlen, U. J. Chem. Phys. 1979, 70, 5045.
- (16) Seelig, A.; Seelig, J. Biochemistry 1974, 13, 4839.
- (17) Seelig, J.; Niederberger, W. J. Am. Chem. Soc. 1974, 96, 2069.
 (18) Seelig, J.; Macdonald, P. M. Acc. Chem. Res. 1987, 20, 221.
- (19) Finkelmann, H.; Ringsdorf, H.; Wendorff, J. H. Makromol. Chem. 1978. 179, 273.
- (20) Emsley, J. W.; Lindon, L. C. NMR Spectroscopy Using Liquid Crystal Solvents; Pregamon Press: Oxford, 1975.
 - (21) Hentschel, R.; Spiess, H. W. J. Magn. Reson. 1979, 35, 157.
 (22) Spiess, H. W. Colloid Polym. Sci. 1983, 261, 193.
- (23) Boddenberg, B.; Grosse, R.; Breuninger, U. Surf. Sci. 1986, 173, L655
- (24) Kelusky, E. C.; Fyfe, C. A. J. Am. Chem. Soc. 1986, 108, 1746. (25) Meirovitch, E.; Samulski, E. T.; Leed, A.; Scheraga, H. A.; Rana-
- navare, S.; Nemethy, G.; Freed, J. H. J. Phys. Chem. 1987, 91, 4840.
- (26) Lifshitz, E.; Goldfarb, D.; Vega, S.; Luz, Z.; Zimmermann, H. J. Am. Chem. Soc. 1987, 109, 7280.
- (27) Stockton, G. W.; Polnaszek, C. F.; Leitch, L. C.; Tullock, A. P.;
 Smith, I. C. P. Biochem. Biophys. Res. Commun. 1974, 60, 844.

(28) Pake, G. E. J. Chem. Phys. 1948, 16, 327.

TABLE I: NMR Line Width and Spin-Lattice Relaxation Data for Various Deuterated Alkyl Modified Silicas

labeled silane	notation	line width ^a	slope ^b
Cl(CH ₃) ₂ Si(CH ₂) ₁₁ CD ₃	12M12	6.5	-1.60 ± 0.01
$Cl(CH_3)_2Si(CH_2)_{10}CD_2CH_3$	12M11	16	-1.60 ± 0.01
Cl(CH ₃) ₂ Si(CH ₂) ₃ CD ₂ (CH ₂) ₅ CH ₃	10M4	40	-0.90 ± 0.01
Cl(CH ₃) ₂ SiCD ₂ (CH ₂) ₅ CH ₃	7 M 1	46	-1.10 ± 0.01
$(CH_3)_3Si(CH_2)_3CD_2(CH_2)_5CH_3$	10 P4		

^a Measured in kHz at the base. ^b Measured from plots of $\ln T_1$ vs 1000/T.

polycrystalline sample in which all orientations of the $C^{-2}H$ bond $(\theta = 0-90^{\circ})$ are equally probable, a uniaxial powder pattern is obtained as shown in Figure 1 which was simulated by using a quadrupole coupling constant of 165 kHz and a natural line width of 0.25 kHz.²⁸ In the powder pattern the singularities with a separation of ${}^{3}/{}_{4}Q_{0}$ arise from bonds perpendicular to the magnetic field ($\theta = 90^{\circ}$ in eq 1) and the $3/2Q_0$ wide shoulders are due to parallel field alignment ($\theta = 0^0$ in eq 1). For aliphatic C-²H bonds where $Q_0 = 165$ kHz, a uniaxial powder pattern with a 123-kHz peak separation and 246-kHz base width is obtained at the rigid limit. In some cases signals from the parallel component are not distinguishable due to noise and natural line broadening.²⁵

In cases other than the rigid limit the presence of motion changes the line shape. In the simplest case where rapid reorientation of the C-2H bond occurs around a well-defined arbitrary axis (unique axis of reorientation) tilted at an angle α relative to the $C^{-2}H$ bond, a uniaxial powder pattern is obtained with reduced quadrupole splitting. This condition is described by eq 2.

$$\Delta \nu = \frac{3}{4}Q_0(\frac{1}{2}(3\cos^2\alpha - 1))$$
(2)

Line shapes obtained from some samples differ substantially because of slow motions with correlation times in the order of the inverse quadrupole coupling constant, the absence of a unique axis of reorientation, or a combination of both.^{29,30} Under these conditions line shapes are sensitive to motional rates and give rise to a series of ²H dynamic line shapes.^{29,30} The overall shapes of the lines may vary from those that are broad and featureless (i.e., Lorentzian lines) to lines that have partially developed splitting patterns.

Experimental Section

Materials. Lithium aluminum deuteride, iodomethane- d_3 , heptanoic acid, 10-undecenoic acid, 10-undecenol, and phosphorus tribromide were obtained from the Aldrich Chemical Co. (Milwaukee, WI). Trichlorosilane and dimethylchlorosilane were purchased from Petrarch Systems, Inc. (Bristol, PA). LiChrosorb SI-60 silica was obtained from EM Science (Cherry Hill, NJ).

Synthesis of Labeled Compounds. An equal molar amount of toluenesulfonyl chloride was added to 10-undecenol which was dissolved in pyridine. The resulting 10-undecenyl tosylate was treated with deuterated lithium dimethyl cuprate to form labeled dodecene. Subsequently, the dodecene was coupled with dimethylchlorosilane under anti-Markovnikov conditions³¹ to produce $Cl(CH_3)_2Si(CH_2)_{11}CD_3$.

10-Undecenoic acid was esterified with methanol in the presence of sulfuric acid. The resulting methyl ester was separated, purified by distillation, and reduced with LiAlD₄ to yield the deuterated alcohol. The alcohol was converted to a tosylate by reacting it with toluenesulfonyl chloride in pyridine. The tosylate was treated with excess $LiCu(CH_3)_2$ in diethyl ether to give $CH_2 = CH(C-CH_3)_2$ H₂)₈CD₂CH₃ which in turn was reacted with dimethylchlorosilane as described above to produce $Cl(CH_3)_2Si(CH_2)_{10}CD_2CH_3$.

Heptanoic acid was reduced with LiAlD₄ to obtain deuterated heptanol, and the alcohol was treated with PBr₃ to produce the

⁽¹²⁾ Gilpin, R. K.; Gangoda, M. E. Anal. Chem. 1984, 56, 1470.

⁽¹³⁾ Gangoda, M. E.; Gilpin, R. K.; Fung, B. M. J. Magn. Reson. 1987, 74, 134.

⁽¹⁴⁾ Beaufils, J. P.; Hennion, M. C.; Rosset, R. Anal. Chem. 1985, 57, 2593.

⁽²⁹⁾ Meirovitch, E.; Freed, J. H. Chem. Phys. Lett. 1979, 64, 311.

⁽³⁰⁾ Davidson, D. W.; Garg, S. K.; Ripmeester, J. A. J. Magn. Reson. 1978, 31, 399.

⁽³¹⁾ Gangoda, M. E.; Gilpin, R. K. J. Labeled Compd. Radiopharm. 1982, 19. 283.



Figure 2. ²H NMR spectra at ambient temperature. Surfaces: (a) 10P4, (b) 12M12, (c) 12M11, (d) 10M4, (e) 7M1.

deuterated bromoalkane. A Grignard reagent was prepared which was reacted with excess dimethyldichlorosilane to form $Cl(C-H_3)_2SiCD_2(CH_2)_5CH_3$.³¹

Subsequently, $Cl(CH_3)_2Si(CH_2)_3CD_2(CH_2)_5CH_3$ was prepared from the above Grignard via treatment with allyl bromide to form CH_2 =CHCH₂CD₂(CH₂)₅CH₃ which was reacted with dimethylchlorosilane as discussed above.

Preparation of Modified Silicas. The above silanes were vacuum distilled and their structure and purity verified by NMR and IR spectrometry. Subsequently, these reagents were reacted with LiChrosorb SI-60 silica (average particle diameter Dp = 10 μ m) under toluene reflux conditions¹² to obtain the chemically modified surfaces. Additionally, trimethyldecylsilane was prepared from Cl(CH₃)₂Si(CH₂)₃CD₂(CH₂)₅CH₃ by treatment with excess methylmagnesium bromide. This unreactive silane was physically coated onto silica by use of a rotary evaporator.³²

Measurements. All NMR spectra were acquired at a 46.1-MHz with a General Electric (Fremont, CA) Model GN-300 NMR spectrometer. The spectra were recorded by using a modified quadruple echo sequence $[(\pi/2)_x-t-(\pi/2)_y]$ where t was 100 μ s and the length of the $\pi/2$ was 2.25 μ s. Spin-lattice relaxation times were measured by using a quadrupole echo inversion recovery pulse sequence.

Results and Discussion

A summary of the labeled silanes used for synthesis of the various surfaces and the notation to identify each are listed in Table I. Representative spectra for the modified materials obtained at ambient temperature appear in Figure 2. Likewise, the corresponding line width data and values for the slopes of plots of the natural logarithm of the spin-lattice relaxation times vs inverse temperature are given in columns three and four, respectively.

The liquidlike resonance (Figure 2a) for the physically coated sample (10P4) reflects a complete averaging of the quadrupole interactions. Likewise, it also demonstrates that line broadening for the chemically attached groups as discussed below is not due

The Journal of Physical Chemistry, Vol. 93, No. 12, 1989 4817

merely to the presence of silica. The deuterium line widths for the chemically modified surfaces were less than that expected for rigid-limit splitting (123 kHz) and ranged from 6.5 to 46 kHz, indicating a partial averaging of the quadrupole interactions.

As shown in Figure 2b-e, the line widths for the chemically attached chains were dependent on the position of labeling. Nearly identical values (46 and 40 kHz, respectively) were observed for the first (7M1) and fourth (10M4) position deuterons whereas decreases in line width were observed toward the chain's end. Line widths for the 12M11 and 12M12 surfaces were 16 and 6.5 kHz, respectively.

The reduced quadrupole splitting which results from free rotations about C-C bonds (tetrahedral angles) is given by

$$\Delta \nu = \frac{3}{4}Q_0(\frac{1}{2}(3\cos^2 109^\circ - 1))^n \tag{3}$$

where n is the number of bond rotations that contribute to the averaging process. The calculated value for averaging from a single rotational process, 44 kHz, is within experimental error identical with that obtained for the 7M1 surface (46 kHz) and only slightly larger than that obtained for the 10M4 surface (40 kHz). The nearly constant values in line width for the first and fourth position deuterons suggest that the motions in this region of the immobilized chains are correlated strongly likely due to tight packing which prevents the chains from behaving as isolated units. Similar trends have been reported for phospholipid bilayers^{15,18} where line width changes little as a function of labeling position for deuterons near the head group and sharply for those toward the tail of the molecule. In those cases where labeling was near the chain's end (i.e., the 12M11 and 12M12), additional motions contributed to the averaging process. Line widths of 6.5 and 16 kHz for the terminal methyl and adjacent methylene deuterons, respectively, indicate that several bond rotations are involved.

A model that fits the above line width data is one where the bonded chains near the surface (i.e., the region of the chains at least through the fourth position) are more rigid and translationally/conformationally dynamic near the chain's end (i.e., at least through three to four bonds from the terminal methyl group). Similar models have been proposed for lipid bilayers.¹⁵

For all cases examined the line shapes were not uniaxial (Lorentzian vs axially symmetric powder patterns) and indicated the presence of complex considerations. Similar Lorentzian line shapes have been reported for polymers,²⁵ liquid crystals,²⁶ and the clathrate hydrate of tetrahydrofuran³⁰ and have been explained in terms of the presence of slow motions and the absence of unique axes of reorientation. In some cases a combination of both arguments has been used. Such a combination provides a reasonable basis for explaining the observed line shapes in the current study. The absence of unique axes of reorientation likely arises from a distribution in chain packing due to the heterogeneous reactivity of the surface.^{33,34} Nonuniformity in the distribution for similar silane modified surfaces has been demonstrated via other spectral techniques such as infrared^{2,3} and luminescence³³ spectrometry. Likewise, Lorentzian line shapes have been reported for silica modified with $Cl(CH_3)_2SiO(CD_2)_nCD_3$.²⁴

In an effort to further elucidate the motional dynamics and changes in motional dynamics along the bonded chains, partially relaxed spectra were recorded on the chemically modified surfaces as a function of temperature by using an inversion recovery pulse sequence. Subsequently, spin-lattice relaxation times (T_1) were calculated. Shown in Figures 3 and 4 are partially relaxed spectra for 12M12 and 7M1 surfaces. In cases where spin-lattice relaxation times differ dramatically for a single-site complex, line shapes are obtained^{24,35} in the partially relaxed spectra. As seen from Figures 3 and 4, the broad resonances do not consist of a superposition of spectra with widely differing T_1 values. However,

(32) Gilpin, R. K.; Gangoda, M. E. Talanta 1986, 33, 176.

⁽³³⁾ Lochmuller, C. H.; Colborn, A. S.; Hunnicutt, M. L.; Harris, J. M. Anal. Chem. 1983, 55, 1344.

⁽³⁴⁾ Claudy, P.; Letoffe, J. M.; Gonnet, C.; Morel, D.; Ramamonjinirina, E.; Serpinet, J. J. Chromatogr. 1985, 330, 227.

⁽³⁵⁾ Gottlieb, H. E.; Luz, Z. J. Magn. Reson. 1983, 54, 257.



Figure 3. Partially relaxed spectra of the 12M12 surface. Delay time (in seconds) between π and $\pi/2$ pulses: (a) 0.003, (b) 0.006, (c) 0.01, (d) 0.017, (e) 0.03, (f) 0.05, (g) 0.09, (h) 0.13, (i) 0.20, (j) 0.35, (k) 0.60.



Figure 4. Partially relaxed spectra of 7M1 surface. Delay time (in seconds) between π and $\pi/2$ pulses: (a) 0.001, (b) 0.003, (c) 0.006, (d) 0.01, (e) 0.017, (f) 0.03, (g) 0.05, (h) 0.09, (i) 0.13, (j) 0.20, (k) 0.35, (l) 0.06.

these data do not preclude some differences in gradation of motions within a narrower range. This would presumably be the case for chains attached under heterogeneous reaction conditions where the bonding density varies.

Changes in T_1 as a function of temperature are summarized in Figure 5 for the chemically modified surfaces. The slopes of



Figure 5. In T_1 vs 1000/T for chemically modified surfaces. Surfaces: (a) 12M12, (b) 12M11, (c) 7M1, (d) 10M4.

linear fits to these data are given in Table I. In each case, T_1 increased with temperature which suggests the relevant molecular motions that contribute to the relaxation process are fast with respect to the Larmor frequency. Similar slopes (-1.60) were observed for 12M12 and 12M11 surfaces and are in good agreement with those reported previously^{13,15} for similar systems. Significantly smaller slopes were observed for both fourth (10M4 surface) and first (7M1 surface) deuterons. However, the value for the slope (-0.90) for fourth position deuterons was smaller than that (-1.10) for the first position deuterons. This reversal also is consistent with differences in motional averaging near the end of the chain compared to those near the anchoring position.

Conclusions

The current investigation demonstrates the potential use of specific deuteration to study various aspects of chemically modified surfaces. Although only the dry state has been examined in the current study, the influence of solvent and secondary modifying reagents on the interfacial properties of various modified silicas can also be examined by using a similar procedure. A number of these studies are now in progress.

Interesting trends have been observed which reflect different motional/conformational processes along the chain. In order to make more quantitative comparisons, the relationship of T_1 vs 1/T (i.e., differences in the slopes from such plots) data from other labeling points within the bound chains is needed. Likewise, information under subambient conditions is also needed. Both of these types of studies are also being carried out.

Acknowledgment. Support from DARPA-ONR Contract N0014-86-K-0772 is acknowledged.