DOE/ER 13835-TF

GRANT NO. DE-FG02-88ER13835

Final Report

to .

Division of Chemical Sciences

Department of Energy

Washington, DC 20545

INSTITUTION: The Pennsylvania State University
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University Park, PA 16802

TITLE: THE FREE-RADICAL AND ION CHEMISTRY OF
SILANES, GERMANES, PHOSPHINES AND RELATED
COMPOUNDS.

PERIOD COVERED: 1965-1994

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Date: May 11, 1995

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Since 1965 with continuous support from the Atomic Energy Commission, Energy Research and Development Administration, and Department of Energy, we have been carrying out a systematic study of the ionic and free radical reactions that occur in the photochemistry and radiation chemistry of hydrides of Groups IV and V of the periodic table, principally silanes, germanes, stannanes and phosphines. In this final technical report, we shall briefly describe high points of this research and cite references to the publications that describe it. Reprints of publications of work published during the past five years are attached as an appendix.

I. Properties and Reactions of Gaseous Ions.

Electron impact and mass spectrometric techniques have been used to study the energetic properties of organosilicon compounds and in this way we have succeeded in determining the dissociation energies of Si-H, Si-C, Si-Si, Si-F, Si-Cl, Si-Br, Si-O, and Si-N bonds in silane, disilane, methylsilane and a series of trimethylsilanes (1,9,11). In addition, a number of bond dissociation energies and free-radical ionization potentials in a series of trimethylstannanes have been measured (1,4,5). These experimental studies formed the basis of a widely read paper (12) in which was proposed a calculational scheme for obtaining standard enthalpies of formation of alkylsilanes. In our studies of the gas-phase ionic chemistry of silanes we have identified and measured rate constants for the elementary reactions in pure SiH_4 (2,14), Si_2H_6 (19), CH_3SiH_3 (11,21), $(\text{CH}_3)_2\text{SiH}_2$ (13), $(\text{CH}_3)_3\text{SiH}$ (13) and $(\text{CH}_3)_4\text{Si}$ (13). We have also identified the ion-molecule reactions (and determined their rate constants) that occur in mixtures of SiH_4 with H_2 (29), CH_4 (3,18,29), C_2H_2 (7,24), C_2H_4 (8,23,31,36), CF_4 (27,28), C_6H_6 (26,30), H_2O (18), $\text{CH}_n\text{Cl}_{4-n}$ ($n=0-3$)(43), and CO (44). These studies demonstrated that the dominant reaction of

positive carbonium ions and hydronium ions with compounds containing a Si-H bond in facile abstraction of a hydride ion with formation of a siliconium ion, viz.

This dominance of hydride abstraction reflects the very strong basic nature of the Si-H bond in the gas phase. Further evidence of this strong gas-phase basicity was provided by our 1968 discovery of the existence of the SiH_5^+ ion (3) and this was followed some five years later by our measurement of the proton affinity of SiH_4 (16), namely 153 ± 3 kcal/mole. In subsequent studies we have demonstrated the existence of GeH_5^+ and determined the proton affinity of GeH_4 to be some 10 kcal/mole stronger than that of SiH_4 (35). Thus GeH_4 is a stronger Bronsted base than C_2H_4 in the gas-phase.

Tandem mass-spectrometric techniques have also been used in studies of the reactions of CH_3^+ ions with a series of methyl (32) and ethyl (33) silanes and of C_2H_5^+ , C_3H_7^+ and C_4H_9^+ ions with methyl- and ethylsilanes (34). The major result of this work was the establishment of the dominant role played by the abstraction of negative alkyl ions by the various carbonium ions. That is, it was found that the following reactions competed on an almost equal basis with hydride in abstraction to form siliconium ions having one less alkyl group than the parent methyl or ethyl silane.

The same general techniques were used to investigate the kinematics of the abstraction of hydride ions from silane and methylsilane by organosilicon ions (20,22). It was demonstrated conclusively that this abstraction does not take place via the generally assumed formation of an intermediate collision complex but rather proceeds by means of a direct process in which the >Si^+ moiety acts simply as a "spectator" to the stripping away of its H^- ion by the attacking organosilicon ion. For example, in the reaction

the product ion, $\text{CH}_3\text{SiD}_2^+$, is formed with essentially thermal kinetic energy (0.04 eV) despite the fact that the kinetic energy of the reactant ion (in the center-of-mass system) was varied from 1.3 to 7.4 eV. This can only mean that no collision complex is formed.

On the other hand, extremely long-lived collision complexes were observed in tandem mass spectrometric studies of the reactions of Si^+ , SiH^+ and SiH_3^+ ions with ethylene (23,31,36,38) and benzene (26,30). These studies were particularly noteworthy because they were among the first reporting direct observation of unstabilized collision complexes (i.e. collision complexes carrying the exothermicity and relative kinetic energy of the collision partners as internal energy). Such long lived complexes appear to be rather unique to organosilicon chemistry because they are not observed under any conditions where C^+ , CH_2^+ and CH_3^+ ions react with ethylene (37). Reactions in which energy-rich collision complexes and their decomposition products are directly observed

simultaneously provide excellent experimental tests of unimolecular reaction rate theory (31,36,38). Moreover, in the long-lived collision complexes of SiH_3^+ ions and benzene, it was demonstrated by isotopic labelling experiments that the ultimate product ion was the phenylsilyl ion and not silatropylium (30), i.e. The reaction was shown to be

Ion-molecule reactions in GeH_4 have also been studied (15,41) and have been found to be similar to those characteristic of SiH_4 . Moreover, it has been demonstrated (41) that GeH_3^+ also forms long-lived collision complexes with C_2H_4 .

II. Photochemical and Free Radical Reactions

Mass-spectrometric techniques have also been used to investigate the gas-phase photochemistry of silanes, methylsilanes, germane, stannane and phosphine.

Although the mercury photosensitized decomposition of SiH_4 had been known since 1932, our work on this system (47,50) was the first to show conclusively that the predominant primary process occurring is the formation of SiH_3 and H via the reactions

and that the energetically more favorable formation of $\text{SiH}_2 + \text{H}_2$ plays only a minor role, if any. It was also demonstrated in these studies that SiH_3 and CH_3SiH_2 free radicals react

with NO via a chain reaction that leads to the formation of H₂, N₂O, SiH₃OSiH₃, SiH₃OSiH₂OSiH₃ and CH₃SiH₂OSiH₂CH₃.

The decomposition of SiH₄, Si₂H₆, CH₃SiH₃, (CH₃)₂SiH₂, (CH₃)₃SiH, (CH₃)₄Si, GeH₄, CH₃GeH₃, (CH₃)₂GeH₂, (CH₃)₃GeH, (CH₃)₄Ge, and (CH₃)₄Sn by H-atom attack has also been investigated and many rate constants at 300K were measured (51,52,54). The only reaction occurring is abstraction of hydrogen from the Si-H, Ge-H and SnH bonds with formation of silyl, germyl and stannyl radicals, respectively. Mass-spectrometric studies of the isotope distribution in the disilane formed by the reaction of SiH₃ and SiD₃ radicals demonstrated clearly that, up to 60 torr total pressure, silyl radicals do not recombine, as do methyl radicals under the same conditions, but rather disproportionate to SiH₂ and SiH₄ (51).

The vacuum-ultraviolet photochemistries of SiH₄ (56), Si₂H₆ (57), CH₃SiH₃ (58), PH₃ (59), GeH₄ (88), SnH₄ (92) and SiH₄-PH₃ mixtures (60) have been studied using the 147 nanometer radiation from a xenon resonance lamp with mass spectrometric monitoring. The principal result of this work has been the demonstration that the predominant primary processes in the vacuum-ultraviolet are those that form a silylene, germylene, or stannylene molecule and a pair of atoms or free radicals, are shown by the following:

In the case of SnH_4 photodecomposition (92) the reaction

is energetically possible and, indeed, appears to play a role of comparable importance to that of $\text{SnH}_2 + \text{H}_2$ formation.

The infrared laser photochemistry of SiH_4 , GeH_4 and PH_3 both by direct multiphoton decomposition (61,64,76,77) and via decomposition initiated by vibrationally excited SiF_4 (63,66,67,77,80,84,85) have been investigated. In these investigations it was shown that SiH_2 , GeH_2 and PH molecules are present and that the monoradicals SiH_3 , GeH_3 and PH_2 and H atoms are absent and that, therefore, the major primary processes are the formation of H_2 and the corresponding diradical SiH_2 , GeH_2 , and PH . This relatively gentle decomposition suggested to us that here was a means to generate these diradicals in the absence of H -atoms and other monoradicals and investigate their reactions with a variety of substrate molecules. Such studies have been carried out with HCl (70), PH_3 (67), GeH_4 (73), NO (78), CH_3Cl (82), H_2 (83), and C_2H_4 (87).

Investigations of the X-ray induced decomposition of silane have led to an elucidation of the mechanisms of the radiolyses of SiH_4 and $\text{SiH}_4\text{-C}_2\text{H}_4$ mixtures (6) as well as of the mechanism of the free-radical scavenging process in irradiated $\text{SiH}_4\text{-NO}$ mixtures (53).

PUBLICATIONS OF F. W. LAMPE OF WORK SUPPORTED BY
AEC, ERDA, AND DOE 1965-1994

A. Properties and Reactions of Gaseous Ions

1. G. G. Hess, F. W. Lampe and A. L. Yergey, "Energetic Properties of Group IV hydrides and Their Alkyl Derivatives by Electron Impact", Ann. N. Y. Acad. Sci. 136, 106 (1966).
2. G. G. Hess and F. W. Lampe, "Ionic Reactions in Gaseous Monosilane", J. Chem. Phys. 44, 2257 (1966).
3. D. P. Beggs and F. W. Lampe, " SiH_5^+ Formation in Ionized CH_4 - SiH_4 Mixtures", J. Chem. Phys. 49, 4230 (1968).
4. A. L. Yergey and F. W. Lampe, "An Electron Impact Study of the Ionization and Dissociation of Trimethylstannanes", J. Organometallic Chem. 15, 339 (1968).
5. F. W. Lampe and A. Niehaus, "Ionization Potentials of Free Radicals Formed by Electron Impact. Methylstannyl Radicals", J. Chem. Phys. 49, 2949 (1968).
6. J. F. Schmidt and F. W. Lampe, "Gamma-ray Radiolysis of Silane and Silane-Ethylene Mixtures", J. Phys. Chem. 73, 2706 (1969).
7. D. P. Beggs and F. W. Lampe, "Ionic Reactions in SiH_4 - C_2H_2 Mixtures", J. Phys. Chem. 73, 3307 (1969).
8. D. P. Beggs and F. W. Lampe, "Ionic Reactions in SiH_4 - C_2H_4 Mixtures", J. Phys. Chem. 73, 3315 (1969).
9. P. Potzinger and F. W. Lampe, "Ionization and Dissociation in SiH_4 and Si_2H_6 ", J. Phys. Chem. 73, 3912 (1969).
10. D. P. Beggs and F. W. Lampe, "Ionic Reactions in SiH_4 - CH_4 and SiH_4 - C_6H_6 Mixtures", J. Phys. Chem. 73, 4194 (1969).
11. P. Potzinger and F. W. Lampe, "Ionic Reactions in CH_3SiH_3 ", J. Phys. Chem. 74, 587 (1970).
12. P. Potzinger and F. W. Lampe, "Thermochemistry of Simple Alkylsilanes", J. Phys. Chem. 74, 719 (1970).
13. P. Potzinger and F. W. Lampe, "Ion-Molecule Reactions in $(\text{CH}_3)_2\text{SiH}_2$, $(\text{CH}_3)_3\text{SiH}$ and $(\text{CH}_3)_4\text{Si}$ ", J. Phys. Chem. 75, 13 (1971).

14. Tung-Yang Yu, T. M. H. Cheng, V. Kempter, and F. W. Lampe, "Ionic Reactions in Monosilane. Radiation Chemistry Implications", J. Phys. Chem. 76, 3321 (1972).
15. J. K. Northrup and F. W. Lampe, "Ionic Reactions in Gaseous Germane", J. Phys. Chem. 77, 30 (1973).
16. T. M. H. Cheng and F. W. Lampe, " SiH_5^+ and the Proton Affinity of SiH_4^+ ", Chem. Phys. Lett. 19, 532 (1973).
17. T. M. H. Cheng, T-Y. Yu and F. W. Lampe, "Ion-Molecule Reaction in Monosilane-Methane Mixtures", J. Phys. Chem. 77, 2587 (1973).
18. T. M. H. Cheng and F. W. Lampe, "Positive-Ion Reactions in Monosilane Water Mixtures", J. Phys. Chem. 77, 2841 (1973).
19. T. M. H. Cheng, T-Y. Yu and F. W. Lampe, "Ion-Molecule Reactions in Disilane", J. Phys. Chem. 78, 1184 (1974).
20. T. M. Mayer and F. W. Lampe, "Kinematics of Hydride Ion and Hydrogen Atom Transfer in Monosilane", J. Phys. Chem. 78, 2195 (1974).
21. T. M. Mayer and F. W. Lampe, "Ion-Molecule Reactions in Methylsilane", J. Phys. Chem. 78, 2422 (1974).
22. T. M. Mayer and F. W. Lampe, "Kinematics of Hydride Transfer Reactions in Methylsilane", J. Phys. Chem. 78, 2429 (1974).
23. T. M. Mayer and F. W. Lampe, "Ion-Molecule Reactions in Monosilane-Ethylene Mixtures", J. Phys. Chem. 78, 2433 (1974).
24. T. M. Mayer and F. W. Lampe, "Ion-Molecule Reactions in Monosilane-Acetylene Mixtures", J. Phys. Chem. 78, 2645 (1974).
25. F. W. Lampe, "Ion-Molecule Reactions in Silane and Organosilane Systems", Ion-Molecule Interactions (P. Ausloos, Editor) Plenum Press, New York 1974, pp. 445-458.
26. W. N. Allen and F. W. Lampe, "Direct Detection of Energy-Rich Collision Complexes in the Reactions of Si^+ , SiH^+ and SiH_3^+ with Benzene", J. Chem. Phys. 65, 3378 (1976).
27. J. R. Krause and F. W. Lampe, "Extensive Redistribution of Fluorine and Hydrogen in the Reaction of CF_3^+ with SiH_4 ", J. Am. Chem. Soc. 98, 7826 (1976).

28. J. R. Krause and F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-CF}_4$ Mixtures", *J. Phys. Chem.* 81, 281 (1977).
29. W. N. Allen, T. M. H. Cheng and F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-D}_2$ Mixtures", *J. Chem. Phys.* 66, 3371 (1977).
30. W. N. Allen and F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-C}_6\text{H}_6$ Mixtures", *J. Am. Chem. Soc.* 99, 2943 (1977).
31. W. N. Allen and F. W. Lampe, "Reactions of Silyl Ions with C_2H_4 . Long-Lived Complexes", *J. Am. Chem. Soc.* 99, 6816 (1977).
32. G. W. Goodloe, E. R. Austin and F. W. Lampe, "Reactions of Methyl Cations with Methyl Silanes", *J. Am. Chem. Soc.* 101, 3472 (1979).
33. G. W. Goodloe and F. W. Lampe, "Reactions of Methyl Cations with Ethyl Silanes", *J. Am. Chem. Soc.* 101, 5649 (1979).
34. G. W. Goodloe and F. W. Lampe, "Reactions of Ethyl, Propyl and Butyl Cations with Methyl and Ethyl Silanes," *J. Am. Chem. Soc.* 101, 6028 (1979).
35. S. N. Senzer, R. N. Abernathy and F. W. Lampe, " GeH_5^+ and the Proton Affinity of Monogermane," *J. Phys. Chem.* 84, 3066 (1980).
36. R. N. Abernathy and F. W. Lampe, "The Role of Collision Complexes in the Reactions of Silyl Ions with Ethylene," *J. Am. Chem. Soc.* 103, 2573 (1981).
37. R. N. Abernathy and F. W. Lampe, "Propyl Ions and Protonated Cyclopropane as Intermediates in the Reaction of Methyl Cations with Ethylene," *Int. J. Mass Spectrom. Ion Phys.* 41, 7 (1981).
38. R. N. Abernathy and F. W. Lampe, "Collisional Moderation by Foreign Gases in the Reaction of SiH_3^+ Ions with C_2H_4 ," *Int. J. Mass Spectrom. Ion Phys.* 51, 3 (1983).
39. S. N. Senzer and F. W. Lampe, "Gaseous Ion Reactions in SiF_4 and $\text{SiF}_4\text{-D}_2$ Mixtures," *J. Appl. Phys.* 54, 3524 (1983).
40. S. N. Senzer, K. P. Lim and F. W. Lampe, "The Reaction of Vinyl Ions with Methane," *J. Phys. Chem.* 88, 5314 (1984).
41. A. Oppenstein and F. W. Lampe, "Ion-Molecule Reactions in Volatile Silanes," *Rev. Chem. Intermed.* 6, 275 (1986).

42. F. W. Lampe, "Mass Spectrometry and Positive Ion-Molecule Reaction in Silanes," in Silicon Chemistry (J. Y. Corey, E. R. Corey, and P. P. Gaspar, Editors), Ellis Horwood Publishers, Chichester, 1988, Chapter 47.
43. K. P. Lim and F. W. Lampe, "The Reactions of Silyl Ions with Chloromethanes," Int. J. Mass Spectrom. Ion Processes **92**, 53 (1989).
44. K. P. Lim and F. W. Lampe, "Ion-Molecule Reactions in SiH_4 -CO Electric Discharges. Formation of the SiC Radical," Int. J. Mass Spectrom. Ion Proc. **101**, 245 (1990).
45. K. P. Lim and F. W. Lampe, "The Reactions of Si^+ Ions with CH_3SiH_3 , CH_3SiD_3 , C_2H_6 and CH_3CHD_2 ," J. Chem. Phys. **96**, 2819 (1992).
46. K. P. Lim and F. W. Lampe, "The Reactions of GeH_3^+ with C_2H_4 ," J. Organic Mass Spec. **28**, 349 (1993).

B. Photochemistry and Free Radical Reactions

47. E. Kamaratos and F. W. Lampe, "Mass-Spectrometric Studies of the $\text{Hg}(^3\text{P}_1)$ Photosensitized Reactions of SiH_4 and CH_3SiH_3 with NO", J. Phys. Chem. **74**, 3939 (1970).
48. H. S. Tan and F. W. Lampe, "Reaction of Ethyl Radicals with Nitric Oxide, Nitrosoethane and Triethylhydroxylamine", J. Phys. Chem. **76**, 3303 (1972).
49. H.S. Tan and F. W. Lampe, "Mass-Spectrometric Studies of the Reactions of Trifluoromethyl Radicals with Nitric Oxide", J. Phys. Chem. **77**, 1335 (1973).
50. E. R. Austin and F. W. Lampe, "Mercury Photosensitized Reactions of Silyl Radicals", J. Photochem. **5**, 155 (1976).
51. E. R. Austin and F. W. Lampe, "Hydrogen-atom Sensitized Decomposition of Monosilane", J. Phys. Chem. **80**, 2811 (1976).
52. E. R. Austin and F. W. Lampe, "Rate Constants for the Reactions of H-Atoms with Silanes and Germanes", J. Phys. Chem. **81**, 1134 (1977).
53. J. P. Bare and F. W. Lampe, "Free radical Chain Formation of Siloxanes in the Radiolysis of SiH_4 -NO Mixtures", J. Phys. Chem. **81**, 1437 (1977).
54. E. R. Austin and F. W. Lampe, "Rate Constant for the Reactions of H-Atoms with Methylgermanes, J. Phys. Chem. **81**, 1546 (1977).

55. G. G. A. Perkins, E. R. Austin and F. W. Lampe, "The 147-Nanometer Photolysis of Hexafluoroacetone", J. Chem. Phys., 68, 4357 (1978).
56. G. G. A. Perkins, E. R. Austin and F. W. Lampe, "The 147-Nanometer Photolysis of Monosilane", J. Am. Chem. Soc. 101, 1109 (1979).
57. G. G. A. Perkins and F. W. Lampe, "The 147-Nanometer Photolysis of Disilane," J. Am. Chem. Soc. 102, 3764 (1980).
58. P. A. Longeway and F. W. Lampe, "The 147-Nanometer Photolysis of Methylsilane," J. Photochem. 14, 311 (1980).
59. J. Blazejowski and F. W. Lampe, "The 147-Nanometer Photolysis of Phosphine and Phosphine-d₃," J. Phys. Chem. 85, 1856 (1981).
60. J. Blazejowski and F. W. Lampe, "The 147-Nanometer Photolysis of Phosphine-Silane Mixtures," J. Photochem 16, 105 (1981).
61. P. Longeway and F. W. Lampe, "The Infrared Multiphoton Decomposition of Monosilane," J. Am. Chem. Soc., 103, 6813 (1981).
62. J. Blazejowski and F. W. Lampe, "Monosilylphosphine Formation by Rapid Silylene Insertion in the Infrared Photodecomposition of Silane-Phosphine Mixtures," J. Photochem. 20, 9 (1982).
63. P. A. Longeway and F. W. Lampe, "The SiF₄-Sensitized Infrared Multiphoton Decomposition of SiH₄," J. Phys. Chem. 87, 354 (1983).
64. J. F. O'Keefe and F. W. Lampe, "Spectroscopic Detection of SiH₂ in the Infrared Multiphoton Decomposition of SiH₄," Appl. Phys. Lett. 42, 219 (1983).
65. R. A. Bernheim, F. W. Lampe, J. F. O'Keefe and J. R. Qualey, "High Vibrational Overtones in SiHCl₃ and SiH₂Cl₂," Chem. Phys. Lett. 100, 45 (1983).
66. J. Blazejowski and F. W. Lampe, "The SiF₄-Sensitized Infrared Multiphoton Decomposition of PH₃," J. Phys. Chem. 88, 1666 (1984).
67. J. Blazejowski and F. W. Lampe, "The SiF₄-Sensitized Infrared Multiphoton Decomposition of PH₃SiH₄ Mixtures," J. Photochem. 24, 235 (1984).
68. R. A. Bernheim, F. W. Lampe, J. F. O'Keefe and J. R. Qualey, "High Si-H Local Model Overtones in SiHD₃," J. Mol. Spectros. 104, 194 (1984).
69. R. A. Bernheim, F. W. Lampe, J. F. O'Keefe and J. R. Qualey, "Visible and Near IR Si-H Vibrational Overtones in SiH₄," J. Chem. Phys. 80, 5906 (1984).

70. C. B. Moore, J. Biedrzycki, and F. W. Lampe, "The Infrared Laser Photochemistry of $\text{SiH}_4\text{-HCl}$ Mixtures," *J. Am. Chem. Soc.* 106, 7761 (1984).
71. J. Blazejowski and F. W. Lampe, "The Frequency and Pressure Dependence of the Absorption of Pulsed CO_2 -Laser Radiation by Phosphine," *J. Photochem.* 29, 285 (1985).
72. R. A. Bernheim, F. W. Lampe, J. F. O'Keefe and J. R. Qualey, III, "Vibrational Overtone Spectra of Methyl Substituted Silanes," *J. Phys. Chem.* 89, 1087 (1985).
73. P. R. Zhu, M. Piserchio and F. W. Lampe, "The Infrared Laser Photochemistry of $\text{SiH}_4\text{-GeH}_4$ Mixtures," *J. Phys. Chem.* 89, 5344 (1985).
74. J. Blazejowski and F. W. Lampe, "The Behavior of PH_3 in a Focused CO_2 -Laser Beam," *J. Appl. Phys.* 59, 2283 (1986).
75. J. Blazejowski and F. W. Lampe, "Remarks on the Behavior of Some Monatomic and Diatomic Gases in an Intense CO_2 -Laser Beam," *Appl. Phys.* B41, 109 (1986).
76. F. W. Lampe, "The Infrared Laser Photochemistry of Silane," *Spectrochimica Acta* A43, 257 (1987).
77. J. Blazejowski and F. W. Lampe, "Absorption of High-Power CO_2 Laser Radiation by SiH_4 , SiF_4 and CH_3PH_2 ," *Spectrochimica Acta* A43, 265 (1987).
78. T. Dohmaru and F. W. Lampe, "Infrared Laser Photochemistry of $\text{SiH}_4\text{-NO}$ Mixtures," *J. Photochem. and Photobiol., A: Chem.* 41, 275 (1988).
79. R. A. Bernheim, D. C. Allbee, F. W. Lampe, J. E. O'Keefe and J. R. Qualey, III, "Visible and Near IR Ge-H Vibrational Overtones in GeH_4 ," *J. Phys. Chem.* 92, 1850 (1988).
80. J. Blazejowski and F. W. Lampe, "The SiF_4 -Sensitized Decomposition of GeH_4 by a Pulsed CO_2 TEA Laser," *J. Phys. Chem.* 93, 8038 (1989).
81. M. V. Piserchio and F. W. Lampe, "The Effect of Nitric Oxide on the Hydrogen-Atom Initiated Decomposition of Monogermane," *Res. Chem. Inter.* 12, 65 (1989).
82. C. B. Moore and F. W. Lampe, "Infrared Laser Photochemistry of $\text{SiH}_4\text{-CH}_3\text{Cl}$ Mixtures," *J. Phys. Chem.* 94, 4094 (1990).

83. J. R. Fisher and F. W. Lampe, "Reactions of Silylene in the Infrared Laser Photochemistry of Monosilane-Deuterium Mixtures," *J. Photochem. and Photobiol.* 51, 301 (1990).
84. J. Blazejowski, J. Rak and F. W. Lampe, "Dynamics of the SiF₄-Sensitized Decomposition of PH₃ by a Pulsed CO₂ TEA Laser," *J. Photochem. and Photobiol., Section A, Chem.*, 52, 347 (1990).
85. J. Blazejowski and F. W. Lampe, "Dynamics of SiF₄-Sensitized Processes Initiated by a Pulsed CO₂ Laser," *Spectrochem. Acta* 46A, 627 (1990).
86. J. Biedrzycki and F. W. Lampe, "Infrared Multiple Photon Decomposition of Si₂F₆ as a Source of SiF₂," *Spectrochem. Acta* 46A, 631 (1990).
87. J. R. Fisher and F. W. Lampe, "Reactions of Silylene in the Infrared Multi-photon Induced Decomposition of Silane-Ethylene Mixtures", *J. Photochem. and Photobiol. A. Chem.* 58, 173 (1991).
88. M. V. Piserchio and F. W. Lampe, "The 147-nm Photodecomposition of Monogermane", *J. Photochem. and Photobiol. A. Chem.* 60, 11 (1991).
89. J. Blazejowski, L. Gruzdięwa, J. Rulewski and F. W. Lampe, "Dependence of the Absorption of Pulsed CO₂-Laser Radiation by SiH₄ on Wavenumber, Fluence, Pulse-Duration, Temperature, Optical Path Length and Pressure of Absorbing and Non-Absorbing Gases," *J. Appl. Phys.*, to appear in May 1995.
90. J. Rak, J. Blazejowski and F. W. Lampe, "The Absorption of Pulsed CO₂-Laser Radiation by CH₃PH₂ as a Function of Wavenumber, Fluence, Pulse-Duration, Temperature, Optical Path Length and Pressure of Absorbing and Non-Absorbing Gases," *J. Photochem. and Photobiol., A: Chem.*, accepted 1995.
91. J. Blazejowski, P. Skuski, and F. W. Lampe, "The Absorption of Pulsed CO₂-Laser Radiation by SiF₄ for Variac Valves of Wavenumber, Fluence, Pulse Duration, Temperature, Optical Path Length, and Pressure of Absorbing and Non-Absorbing Gases," *Appl. Phys. B (Laser and Optics)*, submitted.
92. D. J. Aaserud and F. W. Lampe, "The 147-Nanometer Photodecomposition of SnH₄," in preparation.
93. D. J. Aaserud and F. W. Lampe, "The Thermal Decomposition of Sn₂H₆," in preparation.