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Matrix Reactivity of Zn, Cd, or Hg Atoms (M) in the Presence of Silane: Photogeneration and Characterization of the Insertion Product HMSiH₃ in a Solid Argon Matrix

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Matrix-isolation experiments give evidence that broad-band UV–vis irradiation ($200 \leq \lambda \leq 800$ nm) of an Ar matrix doped with SiH₄ and a group 12 metal atom M (M = Zn, Cd, or Hg) induces metal insertion into an Si–H bond to give the silyl metal hydride molecule HMSiH₃ as the primary product. Si₂H₆ is a second product, irrespective of the identity of M, while the binary hydride MH₂ is also formed when M = Zn or Cd. The products have been identified by their IR spectra and experiments with SiD₄, together with the results of quantum chemical calculations, have provided the means of authentication. The properties of the HMSiH₃ molecules are compared with those of related species, and consideration is given to how the products come to be formed.

I. Introduction

Si–H bond activation in silane molecules urges attention partly in its own right because of the practical importance of the hydrosilation reaction and partly because of the obvious parallels to be drawn with the still greater issue of C–H bond activation.¹ The reaction depends crucially on the initial interaction between the silane and the substrate, and several complexes with SiH₄ or a derivative coordinated to a transition-metal center have been characterized. By contrast, relatively little is known about s- or p-block centers with regard either to their interaction with a silane or to their capacity to activate the Si–H bond.

Matrix isolation^{2,3} has proved a highly informative means of studying weakly bound complexes involving molecules such as SiH₄, H₂, and CO and of charting the reactions they undergo, usually through photoactivation. For example, complexes of SiH₄ with NH₃,⁴ HF,⁵ and HONO⁶ have been characterized in this way. On the evidence of the IR, electron paramagnetic resonance (EPR), and UV–vis spectra, the group 13 metal atoms Al and Ga (M) have also been shown to form loosely bound complexes M···SiH₄, in which the metal atom is η^2 coordinated by the silane.^{7–9} Irradiation at wavelengths near 410 or 254 nm (corresponding to $^2S \leftarrow ^2P$ or $^2D \leftarrow ^2P$ excitation of the metal atom) results in insertion of the metal atom into an Si–H bond to form the M(II) derivative HMSiH₃, a change that can be reversed by exchanging UV for visible photolyzing radiation ($\lambda =$ ca. 580 nm). Under broad-band UV–vis irradiation, however, HMSiH₃ favors an alternative reaction channel that involves cleavage of the M–H bond and formation of the M(I) derivative MSiH₃. Under similar conditions, Hg atoms have also been shown to react with SiH₄ on photoactivation; the primary reaction is again insertion giving HHgSiH₃, but Si₂H₆ is a significant secondary product.¹⁰ By contrast, Si atoms are reported¹¹ to react spontaneously with SiH₄ to produce not only HSiSiH₃ but also its isomer H₂SiSiH₂.

The interaction of Zn, Cd, or Hg atoms with SiH₄ in the gas phase has also been investigated in some detail.¹² Here, excitation of the metal atom to its 3P or 1P state brings about a reaction to produce not HMSiH₃ but the fragments $\bullet MH$ and $\bullet SiH_3$. The vibrational and rotational properties of the $\bullet MH$ radical point to a mechanism in which the M (3P) atom inserts into an Si–H bond with little or no activation barrier to form a bent triplet intermediate $[H-M-SiH_3]^*$; this is too short lived for statistical population of all degrees of freedom and may in fact decompose to $\bullet MH$ and $\bullet SiH_3$ within one skeletal-bending vibration. Ab initio and density-functional theory (DFT) calculations of the appropriate potential-energy surfaces support these conclusions.¹³

Such differences in the outcome of gas and matrix reactions are familiar enough.³ As part of our systematic studies of the thermally and photolytically induced matrix reactions of the group 12 metal atoms Zn, Cd, and Hg, we have now added SiH₄ to a list of simple substrate molecules that has hitherto included H₂,¹⁴ CH₄,¹⁵ HCl,¹⁶ and H₂O.¹⁷ Reactions have been tracked and products identified by the IR spectra of Ar matrixes containing the reagents; the conclusions are endorsed by the observed effects of perdeuteration of the SiH₄ and by the results of DFT calculations. No sign of a weakly bound complex M···SiH₄ (M = Zn, Cd, or Hg) is detectable in the initial deposits, but broad-band photolysis ($200 \leq \lambda \leq 800$ nm) gives rise to the seemingly photostable insertion product HMSiH₃, together with Si₂H₆ as a secondary product. The behavior of the group 12 metal atoms is compared with that of Al and Ga in similar circumstances,^{7–9} and the properties of HMSiH₃ are analyzed in the light of what is known about related metal hydrides.

II. Experimental and Theoretical Procedures

Zinc (Aldrich, purity 99.999%) and cadmium (Aldrich, purity 99.9998%) were each evaporated from a tantalum Knudsen cell that was heated resistively to ca. 300 and 250 °C, respectively, to generate the metal atoms in their ground electronic state. Mercury atoms were generated simply by heating a reservoir of doubly distilled mercury to 40–50 °C. An alternative source of the metal atoms, including some in excited electronic states,

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involved the use of a microwave-powered reactive resonance lamp, as described previously.^{14,15} SiH₄ was synthesized by the action of LiAlH₄ on SiCl₄ in Et₂O solution and purified by fractional condensation in vacuo¹⁸ or used as supplied by Aldrich (99.9%). SiD₄ was prepared from LiAlD₄ and SiCl₄ and purified in a similar manner, or used as supplied by CDN Isotopes (98 atom % D). Argon, nitrogen, and krypton were used as supplied by BOC (research grade).

The metal vapor was co-deposited with an excess of argon doped with either SiH₄ or SiD₄ on a CsI window cooled normally to ca. 12 K by means of a Displex closed-cycle refrigerator (Air Products model CS202). Details of the apparatus are given elsewhere.¹⁹ The matrix gas doped with SiH₄ or SiD₄ to levels varying between 0.1 and 10% was deposited at a rate of 1.0–1.5 mmol h⁻¹, typically over a period of 1.5–2 h. Following deposition, the IR spectrum of the resulting matrix was recorded. The sample was then exposed to the radiation from a Spectral Energy Hg–Xe arc lamp operating at 800 W. A water filter was used to absorb IR radiation and so reduce any heating of the matrix, while the effects of selective photolysis were investigated with the aid of a range of filters: Pyrex ($\lambda > 290$ nm), soda glass ($\lambda > 310$ nm), “vis block” ($\lambda = 200$ –400 nm), UV block ($\lambda > 400$ nm), and Oriel interference filters for $\lambda = 313$ nm (full width at half height (fwhh) 16 nm) and 254 nm (fwhh 10 nm).

IR spectra were recorded in the range 4000–400 cm⁻¹, typically at a resolution of 0.5 cm⁻¹ and with a wavenumber accuracy of ± 0.1 cm⁻¹, with a Nicolet Magna-IR FTIR spectrometer operating with a liquid N₂ cooled MCTB detector. UV–vis spectra were recorded in the range 300–900 nm using a Perkin-Elmer-Hitachi Model 330 spectrophotometer.

DFT calculations were carried out using the Gaussian 98 program suite.²⁰ The method applied throughout was B3LYP with a CEP-31G basis set,¹⁶ a combination that has been shown to give satisfactory results for small molecules of the type described here.

III. Results

The IR spectra associated with the products of the reactions of the metal atoms with SiH₄ and SiD₄ will be reported in turn for Zn, Cd, and Hg. Bands have been assigned on the basis of the following criteria: (i) their growth or decay characteristics under different conditions; (ii) comparisons with the spectra registered in control experiments and with the spectra of related species; (iii) the observed effects of exchanging SiH₄ for SiD₄; and (iv) consideration of how well the measured spectra are reproduced by the results of DFT calculations for a particular product.

Zinc. Various experiments were carried out with thermally generated Zn atoms being co-deposited with an excess of SiH₄-doped argon. The IR spectrum of the deposit consisted only of absorptions attributable to isolated SiH₄ molecules,²¹ as well as weak features associated with trace impurities (H₂O,²² [H₂O]_n,²² CO₂,²³ CO,²⁴ and Zn·OH₂)^{17,25} that could be kept to a minimum but never wholly eliminated. By contrast with similar experiments involving Al or Ga atoms,^{8,9} no additional bands could be discerned as a result of the inclusion of Zn atoms in the matrix. Even matrixes containing only 0.1% SiH₄, which displayed sharp, well-resolved bands, gave no hint of shoulders or satellites attributable to Zn···SiH₄ contact pairs. In this respect, the behavior parallels that of Zn atoms with CH₄¹⁵ but not with HCl¹⁶ and H₂O,^{17,25} which give clear signs of perturbation in the immediate presence of the metal atoms.

Exposure of the matrix to broad-band UV–vis irradiation ($200 \leq \lambda \leq 800$ nm) for as little as 1 min led, as illustrated in

Figure 1, to the appearance of new IR absorptions; details are given in Table 1. The features are concentrated in three main regions: (i) 1820–1880 cm⁻¹; (ii) 930–950 cm⁻¹; and (iii) 825–880 cm⁻¹. The first of these regions is characteristic of the $\nu(\text{Zn–H})$ vibrations of HZnX species in which the substituent X is relatively electropositive (cf. ZnH₂ 1870.2,¹⁴ HZnCH₃ 1866.1,¹⁵ HZnCl 1952.3,¹⁶ and HZnOH 1955.0 cm⁻¹).^{17,25} However, recent studies of the reactions of laser-ablated Si atoms with H₂²⁶ suggest that it may also accommodate $\nu(\text{Si–H})$ vibrations of anionic silicon hydrides, with wavenumbers of 1856/1837 and 1823 cm⁻¹ being attributed to SiH₃⁻ and SiH₂⁻, respectively. Both the second and third regions are most obviously linked with $\delta(\text{SiH}_n)$ modes of one sort or another^{26,27} (cf. the following observed wavenumbers (in cm⁻¹): SiH₃ 923.9,²⁶ Si₂H₆ 938, 834,^{10,26} HAlSiH₃ 846.2,⁹ HGaSiH₃ 845.0;⁹ and the calculated values: SiH₃⁻ 956.6, 868.4,²⁶ SiH₂⁻ 963.1.²⁶ In addition, a very weak absorption was observed to grow at 630.2 cm⁻¹; in that it correlated with a weak absorption at 1870.8 cm⁻¹, this appeared to confirm the presence of ZnH₂ as a minor photoproduct.¹⁴ Extending the period of photolysis to ca. 2 h led to the continuing buildup of the main bands at ca. 1840, 940, 860, and 835 cm⁻¹; there was a simultaneous growth of the satellites appearing on the low-wavenumber flanks of the 1840 and 860 cm⁻¹ bands but at a distinctly slower rate.

Several experiments were attempted in which the photolyzing radiation was confined to a narrower band of wavelengths. Hence it was shown that radiation with $\lambda = 290$ –400 nm was effective in promoting the changes described above, although the use of a filter necessarily restricted the flux of active radiation and so reduced the yield of products in a given time. Irradiation with visible light ($\lambda > 400$ nm) had no effect on the matrix, either before or after UV photolysis. Experiments with low matrix concentrations of metal and SiH₄ were unable to exploit fully the superior definition of the IR bands because the products were then liable to be formed at concentrations too low for ready detection.

Similar experiments were carried out with SiD₄ in place of SiH₄. Hence it was found that all the product features in the IR spectra reported above were strongly redshifted (see Table 1), the three main regions of absorption now (i) 1310–1330, (ii) 680–690, and (iii) 610–640 cm⁻¹, giving H/D ratios of ca. 1.389:1, 1.373:1, and 1.36:1, respectively. The group of absorptions at highest wavenumber is thus more likely to be due to $\nu(\text{Zn–H})$ (for which H/D is typically 1.38–1.39:1)^{14–17,26} than to $\nu(\text{Si–H})$ vibrations (for which H/D is typically ca. 1.37:1).^{26,27}

To complement the studies with thermally generated Zn atoms, some experiments were also carried out with a microwave-powered resonance lamp as a source of the metal atoms in their electronic ground as well as excited states. The IR spectrum of the matrix recorded immediately after deposition of these atoms with an SiH₄/Ar sample was notable for including bands at 1870.8 and 630.2 cm⁻¹ associated with ZnH₂ and also at 935–950 and ca. 835 cm⁻¹. At this stage however, there were only traces of the absorptions at 1820–1850 or 850–880 cm⁻¹ that were the most prominent signs of UV photolysis of a similar matrix including thermally evaporated atoms. Only on broad-band photolysis ($200 \leq \lambda \leq 800$ nm) did these particular features develop to produce something approaching the pattern observed on photolysis of matrixes containing thermally generated Zn atoms.

Cadmium. Figure 2 shows the IR spectra recorded in an experiment in which thermally evaporated Cd atoms were co-deposited with SiH₄-doped Ar (Ar/SiH₄ = 100:1); details of

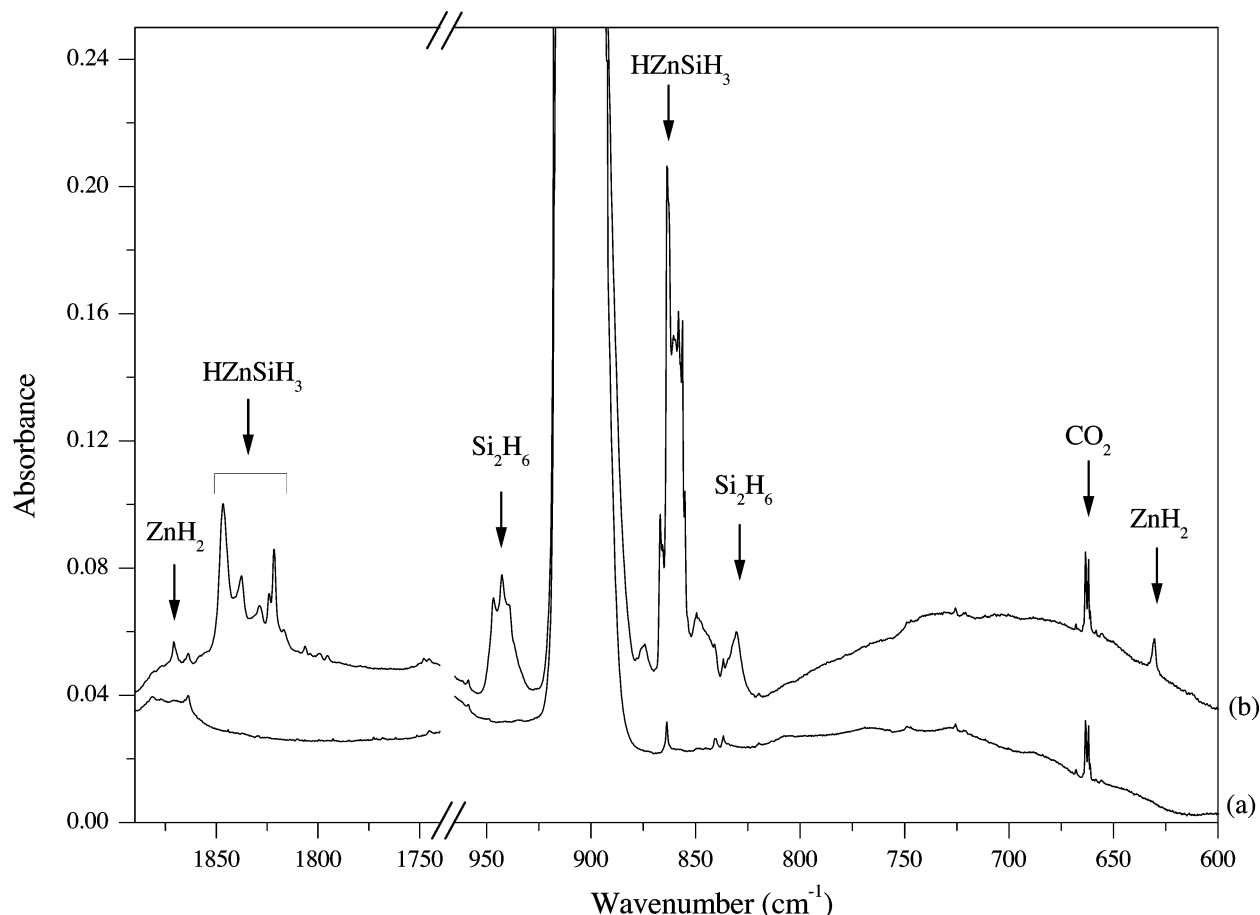


Figure 1. (a) IR spectrum of the deposit formed by cocondensing Zn atoms with a 1% mixture of SiH₄ in Ar at 12 K, and (b) IR spectrum of the same deposit after broad-band UV–vis photolysis.

TABLE 1: Wavenumbers (cm⁻¹) of IR Absorptions Observed Following UV Photolysis of an Ar Matrix Containing Zn Atoms and SiH₄ or SiD₄

Zn/SiH ₄	Zn/SiD ₄	identity
1955.0		HZnOH ZnH ₂
1870.8		
1846.6	1329.8	HZnSiH ₃
1837.7	1324.0	
1828.5	1317.2	
1824.0	1312.6	
1821.6		impurity ^a
1253.8		
946.9	690.1	Si ₂ H ₆
943.0	686.4	
939.5		HZnSiH ₃
874.2		
867.0	639.9	impurity ^a
863.9		
860.4	637.5	HZnSiH ₃
858.2		
856.4		
855.2		
836.9	615.5	Si ₂ H ₆
830.5	614.5	
630.2		ZnH ₂

^a Feature common to Zn and Cd experiments.

wavenumbers are given in Table 2. After deposition, the matrix displayed no IR bands that could not be ascribed to free SiH₄ or trace impurities. After only 1 min of broad-band UV–vis photolysis ($200 \leq \lambda \leq 800$ nm), however, several new bands appeared and grew on continued irradiation. As in the Zn experiments, these were confined mainly to three regions, viz., (i) 1700–1760 cm⁻¹, (ii) 930–950 cm⁻¹, and (iii) 830–870 cm⁻¹. The bands at highest wavenumber, appreciably redshifted

from their counterparts in the Zn experiments, are most likely to be due to $\nu(\text{Cd–H})$ modes (cf. CdH₂ 1753.5,¹⁴ HCdCH₃ 1760.5,¹⁵ HCdCl 1835.8,¹⁶ HCdOH 1837.0 cm⁻¹).¹⁷ Indeed, a feature at 1753.8 cm⁻¹, together with a weak doublet at 604.4/601.7 cm⁻¹, is identifiable with the presence of the CdH₂ molecule.¹⁴ The regions 930–950 and 830–870 cm⁻¹ match closely those in the Zn experiments, and the relevant signals originate most probably in $\delta(\text{SiH}_3)$ vibrations. The close parallel between the behaviors of Zn and Cd makes it unlikely that silicon hydride anions (expected to absorb at 1920–1860 cm⁻¹)²⁶ contribute to either set of spectra. The parallel extended to the behavior of the Cd/SiH₄ matrix on continued photolysis, which led to the growth of the main bands at ca. 1740, 940, 860, and 835 cm⁻¹ but to a slower buildup of the satellites to low wavenumbers of 1740 and 860 cm⁻¹.

The same results could be achieved rather slower on selective photolysis with light having $\lambda = \text{ca. } 313$ nm. Moreover, the products showed no signs of photolability, either on continued UV irradiation or on exposure to visible light ($\lambda = 400\text{--}800$ nm).

Substitution of SiD₄ for SiH₄ resulted in marked redshifts of all the major IR bands arising from photoproducts, with those at 1700–1760 moving to 1220–1270 cm⁻¹ (H/D = 1.39–1.40:1), those at 930–950 to ca. 690 cm⁻¹ (H/D = 1.38:1), and those at 830–870 to 610–640 cm⁻¹ (H/D = 1.345:1). The results of deuteration are thus wholly consistent with the attribution of the original bands to either $\nu(\text{Cd–H})$ or $\delta(\text{SiH}_3)$ fundamentals.

Introduction of the Cd vapor not from a Knudsen cell but from a resonance lamp gave matrixes which showed evidence

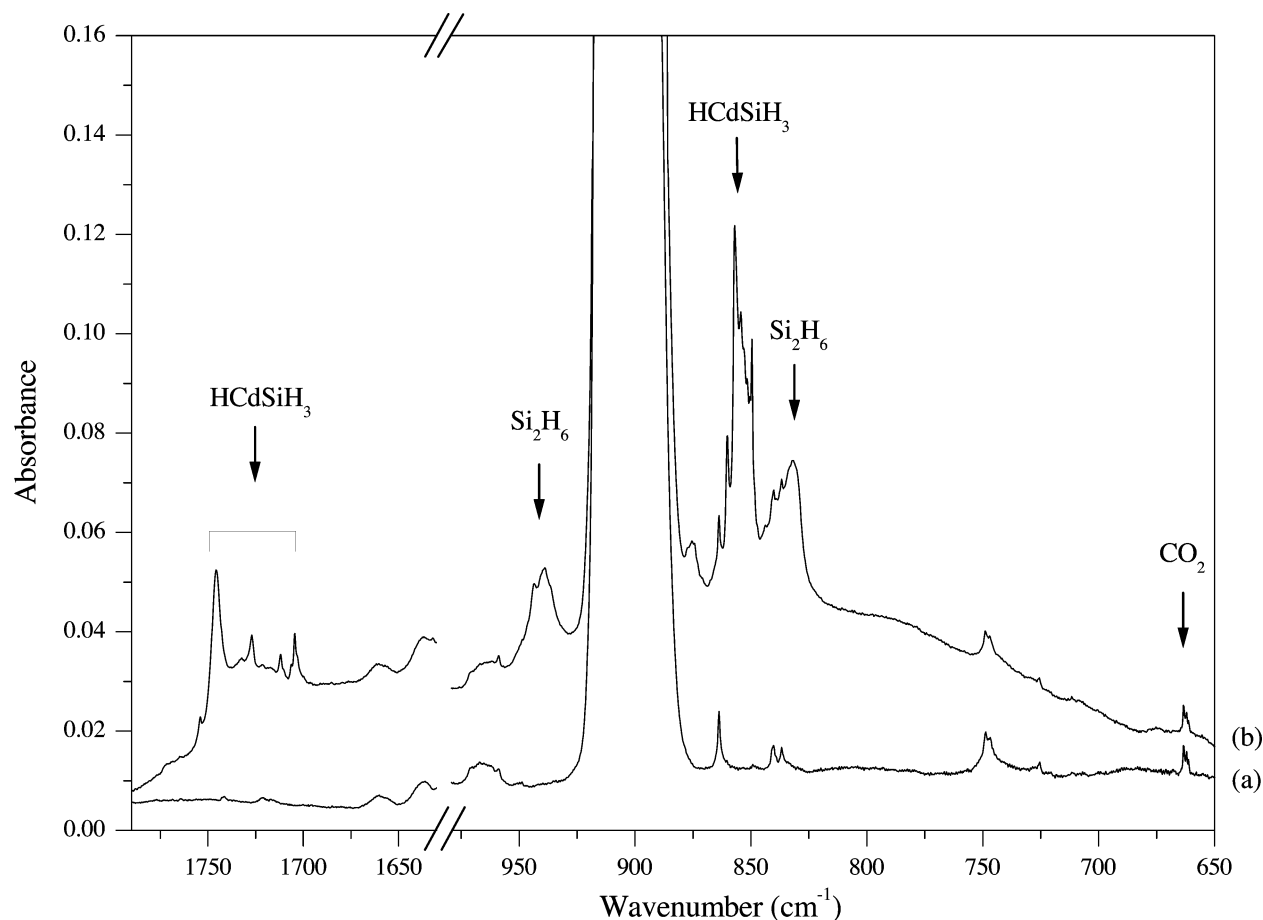


Figure 2. (a) IR spectrum of the deposit formed by cocondensing Cd atoms with a 1% mixture of SiH₄ in Ar at 12 K, and (b) IR spectrum of the same deposit after broad-band UV–vis photolysis.

TABLE 2: Wavenumbers (cm⁻¹) of IR Absorptions Observed Following UV Photolysis of an Ar Matrix Containing Cd Atoms and SiH₄ or SiD₄

Cd/SiH ₄	Cd/SiD ₄	identity
1837.0		HCdOH
1753.8	1264.8	CdH ₂
1745.9	1252.4	HCdSiH ₃
1733.9	1240.6	
1726.8	1229.1	
1712.0	1224.1	
1704.2		
1253.6		impurity ^a
943.5	690.5	Si ₂ H ₆
939.2	687.0	
864.0		impurity ^a
860.2	639.5	HCdSiH ₃
857.0	637.6	
854.3	635.1	
849.7	633.0	
836.4	620.9	Si ₂ H ₆
831.7	616.3	
604.4		CdH ₂
601.7		

^a Feature common to Zn and Cd experiments.

of reaction with SiH₄ on deposition. Thus, the IR spectrum of a matrix prepared in this way exhibited bands characteristic of CdH₂.¹⁴ In addition, the bands centered at ca. 938 and 835 cm⁻¹ were relatively prominent compared with those at 1700–1750 and 840–870 cm⁻¹. However, subsequent broad-band UV–vis photolysis led to the progressive buildup of the latter features and the ultimate development of a spectrum analogous to that observed with thermally generated metal atoms.

In the case of the Zn/SiH₄ experiments, no useful information could be gleaned from measurements of the UV–vis spectrum of the Ar matrix that were effectively limited by a short-wavelength cutoff of ca. 300 nm. Similar measurements on a matrix containing thermally generated Cd atoms revealed a UV absorption near 310 nm attributable to the ³P ← ¹S transition of atomic Cd.^{14,15} Significantly, the presence of SiH₄ appeared to produce a broadening of the band but no change in its position. By contrast, the ²S ← ²P transition of atomic Al in similar circumstances is redshifted by some 45 nm.^{8,9} Any interaction between SiH₄ and the group 12 metal atom in its ground electronic state must therefore be very weak. As noted above, selective irradiation into the ³P ← ¹S absorption band of Cd with light having λ = ca. 313 nm induced the growth of the IR bands at 1700–1760, 930–950, and 830–870 cm⁻¹.

Mercury. Photoexcitation of Hg atoms to the ³P₁ electronic state in the presence of SiH₄ in a solid inert matrix at low temperatures has been shown previously¹⁰ to result in insertion into an Si–H bond. In addition to HHgSiH₃, the primary product thus formed, Si₂H₆ emerges as a significant secondary product. We have carried out experiments along the lines described in the preceding sections by substituting thermally generated Hg for Zn or Cd vapor. The IR spectrum of the Ar matrix initially formed gave no hint of a spontaneous reaction between SiH₄ and Hg atoms in their ground electronic state. On the other hand, broad-band UV–vis irradiation of the matrix gave rise to the IR results illustrated in Figure 3 and detailed in Table 3. New bands appeared and grew with continued photolysis near 1887, 940, 870, and 835 cm⁻¹. Similar findings were reported earlier¹⁰ on the basis of photoexcitation with the output from either a

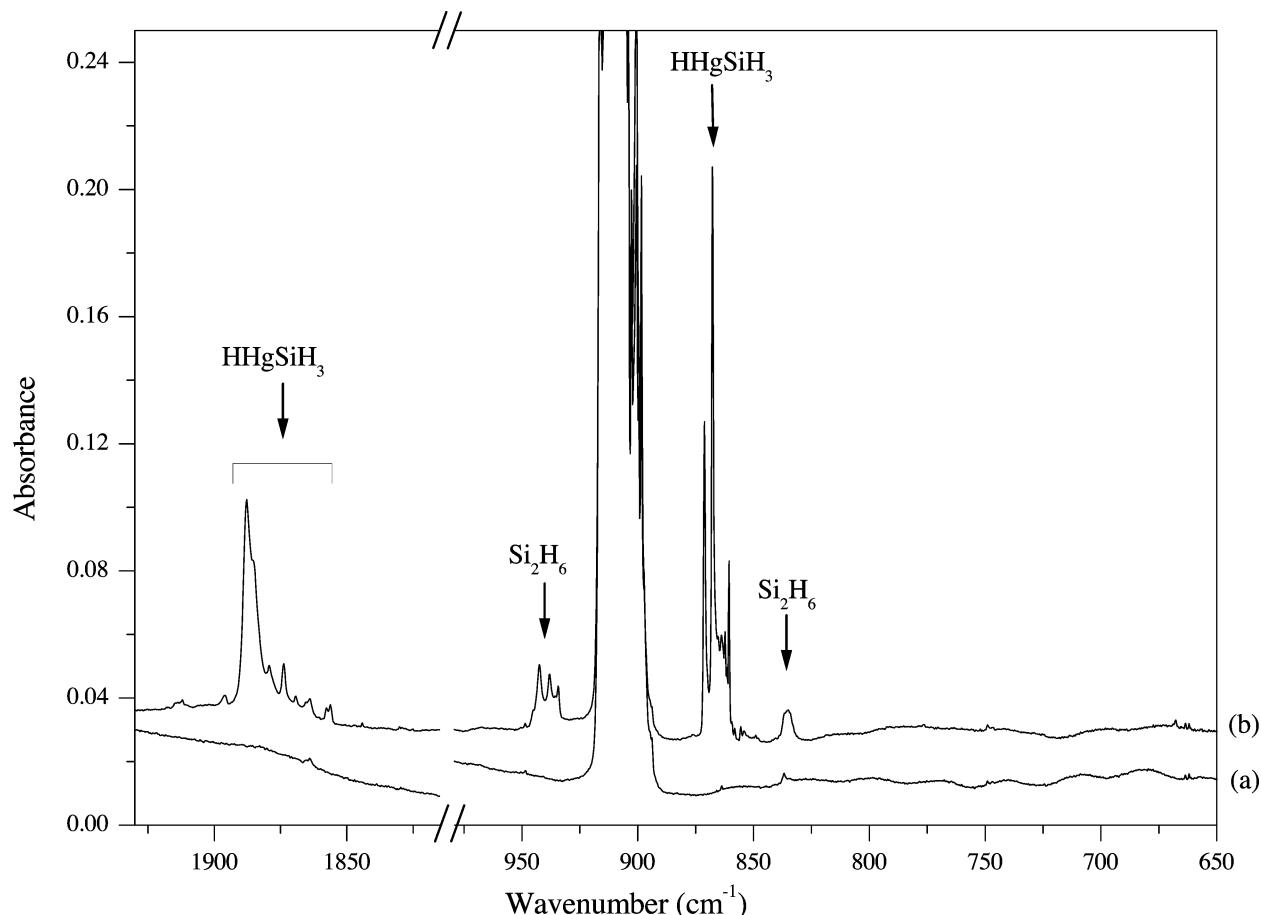


Figure 3. (a) IR spectrum of the deposit formed by cocondensing Hg atoms with a 1% mixture of SiH₄ in Ar at 12 K, and (b) IR spectrum of the same deposit after broad-band UV–vis photolysis.

TABLE 3: Wavenumbers (cm⁻¹) of IR Absorptions Observed Following UV Photolysis of an Ar Matrix Containing Hg Atoms and SiH₄ or SiD₄

Hg/SiH ₄	Hg/SiD ₄	identity
1886.7	1354.4	HHgSiH ₃
1875.9	1332.0	
941.9	690.9	
937.8	687.4	Si ₂ H ₆
871.2	647.7	
867.7	645.7	HHgSiH ₃
862.3	643.3	
860.6		
836.6	624.9	Si ₂ H ₆
833.8	616.4	

deuterium lamp or a KrF excimer laser. In that case, the features near 1887 and 870 cm⁻¹ were associated with the insertion product HHgSiH₃ and those near 940 and 835 cm⁻¹ with Si₂H₆. The results of our experiments with Hg differed somewhat from those of the corresponding experiments with Zn and Cd in that there was no sign of the binary mercury hydride HgH₂²⁸ and the IR bands near 940 and 835 cm⁻¹ appeared to be significantly weaker compared with those at high wavenumber (1700–1900 cm⁻¹) and near 870 cm⁻¹. In keeping with the previous report,¹⁰ the main bands near 1887, 940, 870, and 835 cm⁻¹ built up on continued photolysis, but the weaker features near 1875 and 860 cm⁻¹ grew more slowly.

Selective photolysis of the initial Hg/SiH₄-doped matrix with radiation having $\lambda = \text{ca. } 254 \text{ nm}$ produced similar results, albeit at a reduced rate of product growth. By contrast, visible radiation had no effect either before or after exposure to UV photolysis. All the product bands showed a pronounced redshift when SiH₄

gave way to SiD₄ with H/D ratios varying from 1.393:1 to 1.344:1 (see Table 3) and thereby helping to identify the nature of the vibration as well as the carrier of the absorption (q.v.).

As in the studies with Zn and Cd, introduction of the Hg vapor from a resonance lamp caused some reaction with SiH₄ to occur during deposition of the Ar matrix. The IR spectrum of the resulting deposit then included the absorptions near 940 and 835 cm⁻¹, but of the absorptions at ca. 1880 and 870 cm⁻¹, there was no sign. Only on UV photolysis of the matrix were these features observed to develop.

IV. Discussion

The reactions of group 12 metal atoms with both methane and silane have attracted interest not only through experimental studies^{3,10,12,15} encompassing the gaseous as well as the matrix phases but also through quantum chemical analysis.^{12,13} As described above, new IR features are seen to develop as a result (a) of photolytically induced reactions between SiH₄ and Zn, Cd, or Hg atoms (M) isolated together in a solid Ar matrix or (b) of cocondensation of the same metal atoms from a reactive resonance lamp with an excess of SiH₄-doped Ar. The main products will be shown to be the silyl metal hydride, HMSiH₃, formed by insertion of the electronically excited M atom into an Si–H bond, and disilane, Si₂H₆, in proportions that vary with the conditions of formation. Analogous studies of the systems M/HCl,¹⁶ M/H₂O,^{17,25} and M'/SiH₄^{8,9} (M = Zn, Cd, or Hg; M' = Al or Ga) have provided clear spectroscopic evidence that the metal atom in its ground electronic state adds to the substrate to form a loosely bound preinsertion complex. Unlike the group 13 metal atoms Al and Ga,^{8,9} the group 12 metal atoms show

TABLE 4: Reaction Energies, ΔE in kJ mol⁻¹, Calculated for Selected Changes Involving M (Zn, Cd, or Hg) and SiH₄^a

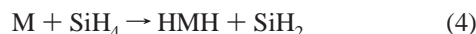
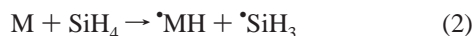
change	M = Zn	M = Cd	M = Hg
M (¹ S) → M (³ P)	+410 ^a /391 ^b	+385 ^a /374 ^b	+495 ^a /500 ^b
M (³ P) + SiH ₄ → HMSiH ₃ (³ A)	-138	-96	-170
M (³ P) + SiH ₄ → HMSiH ₃ (¹ A ₁)	-397	-335	-415
M (³ P) + SiH ₄ → MH [•] + [•] SiH ₃	-127 ^a /96 ^b	-87 ^a /64 ^b	-165 ^a /151 ^b
M (³ P) + SiH ₄ → H [•] + [•] MSiH ₃	-78	-46	-132
M (³ P) + SiH ₄ → HMH + SiH ₂ (³ A ₁)	-91	-21	-103

^a Basis set CEP-31G. ^b Experimental value.^{13a}

no sign of forming such a complex with SiH₄. Accordingly, we consider first the potential for interaction with Zn, Cd, or Hg atoms before going on to analyze the properties of the HMSiH₃ molecules and the likely mechanisms controlling the formation of these and Si₂H₆.

M^{•••}SiH₄. Our DFT calculations using the B3LYP method confirm expectations and the results of earlier calculations involving both CH₄²⁹ and SiH₄¹³ that in its ¹S ground electronic state a Zn, Cd, or Hg atom is incapable of activating the SiH₄ molecule. With unrestrained geometry, only very shallow potential-energy minima can be found for the M (¹S)^{•••}SiH₄ assembly with depths calculated not to exceed 1 kJ mol⁻¹. The only significant interaction, occurring between the valence ns orbital of M and the bonding t₂ orbitals of the SiH₄, can lead only to full occupation of bonding and antibonding MOs and no net bonding. The situation is not unlike that between a noble gas and SiH₄, with neither component able to offer occupied or vacant orbitals of suitable energy to provide a useful basis for a specific donor–acceptor interaction. This contrasts with the behaviors of M (¹S) atoms in the presence of HCl¹⁶ and H₂O¹⁷ in similar circumstances; vibrational perturbation of these substrates attests to the formation of loosely bound M^{•••}HCl and M^{•••}H₂O adducts. SiH₄ is capable of forming such adducts with ground-state (²P) Al and Ga atoms.^{8,9} Coordination of the metal via an edge of the SiH₄ tetrahedron is then calculated to result in a binding energy of ca. 10 kJ mol⁻¹, with the perturbation leading to a slight distortion and measurable shifts of the vibrational fundamentals of the SiH₄ molecule under appropriate conditions of matrix isolation. In keeping with the reduced basicity of the group 12 metals and theoretical forecasts, however, our experiments with Zn, Cd, or Hg under the same conditions were unable to detect any comparable IR features.

None of the possible reactions 1–4 between SiH₄ and a metal atom M = Zn, Cd, or Hg is predicted by either present or earlier¹³ studies to be exothermic when M is in its ¹S ground electronic state. Clearly, therefore, energy has to be injected if any such change is to occur. There is now ample theoretical evidence that excitation of M to its lowest-lying excited state,



³P, gives rise to an exciplex M^{••}•SiH₄, now with a significant binding energy and also with the thermodynamic potential to undergo many of the reactions 1–4 (see Table 4). Moreover, there appears to be little or no barrier to the breaking of the Si–H bond. Depending on M and the conditions, this may lead initially to an HMSiH₃ intermediate in a ³A' excited state, having a highly angular H–M–Si skeleton and an M–H bond length very similar to that of the free [•]MH molecule. Of the channels open to this excited molecule, the thermodynamically most

TABLE 5: Calculated Bond Lengths (Å) and Angles (deg) of Equilibrium Geometries of HMSiH₃ Molecules^a

fragment	M = Zn	M = Cd	M = Hg
H–M	1.5545	1.7127	1.6962
M–Si	2.3836	2.5495	2.5311
Si–H	1.5159	1.5158	1.5134
M–Si–H	106.18	106.18	106.97
H–Si–H	112.58	112.59	111.87

^a Basis set CEP-31G, symmetry C_{3v}.

favorable option involves relaxation to the singlet (¹A₁) ground state, which is characterized by a linear H–M–Si skeleton (thereby completing reaction 1). On the other hand, calculations indicate that little or no barrier opposes the dissociation of HMSiH₃ (³A') into [•]MH and [•]SiH₃, which are the products observed in experimental studies of the interaction between M (³P) and SiH₄ in the gas phase (reaction 2).^{3,10,12,13} Of the reaction channels 3 and 4, no direct experimental evidence has yet come to light.

HMSiH₃ (¹A₁). DFT calculations using the B3LYP functional find an equilibrium geometry with C_{3v} symmetry for each of the molecules HMSiH₃ in its singlet ground state. The dimensions and wavenumbers and intensities in IR absorption of the fundamental vibrational transitions calculated for both HMSiH₃ and DMSiD₃ are given in Tables 5 and 6; the results for HMSiH₃ are close to those reported previously by Alikhani.¹³ The most intense IR absorptions are predicted to correspond to the ν(M–H) (ν₂) and symmetric δ(SiH₃) (ν₃) modes with wavenumbers of 1700–1900 and ca. 830 cm⁻¹, respectively. Next in order of intensity are the ν(Si–H) modes (ν₁ and ν₅) at 2100–2200 cm⁻¹, δ(SiHM) (ν₈) at 300–400 cm⁻¹, and antisymmetric δ(SiH₃) (ν₆) near 920 cm⁻¹. However, the earlier experience of Legay-Sommaire and Legay¹⁰ with matrix-isolated HHgSiH₃ is that the proximity of ν₁ and ν₅ to the ν₃ (t₂) absorption of the much more abundant SiH₄ precursor is liable in practice to prevent them from being observed. The ν₈ absorption is predicted to be less than one-fifth the intensity of the strongest absorption (due to ν₂) as well as occurring in a region of reduced detector sensitivity. The remaining fundamentals ν₆, ν₇, and ν₄ are expected to have IR intensities that decrease in that order, being at least 1 order of magnitude weaker than the strongest absorption.

On this basis, the two regions of strongest IR absorption that were observed to develop at 1700–1900 and 850–880 cm⁻¹ on UV irradiation of an Ar matrix containing SiH₄ and Zn, Cd, or Hg atoms are most plausibly identified with ν₂ and ν₃ of the appropriate insertion product HMSiH₃. Such an inference is supported not only by the effects of deuteration but also by the clear parallels that can be drawn with the earlier study of the Hg/SiH₄ system.¹⁰ Despite every endeavor, no sign of the ν(Si–H) or ν(Si–D) fundamentals ν₁ and ν₅ could be elicited for any of the molecules, the relevant features being obscured presumably by the much stronger absorption due to ν₃ (t₂) of the parent silane molecule.²¹ No similar problem beset the detection of the ν₈ mode, and the failure to discern any feature

TABLE 6: Comparison of Calculated and Observed Wavenumbers (cm⁻¹) for HMSiH₃ Molecules: Calculated Intensities (km mol⁻¹) in Parentheses

metal	mode	SiH ₄		SiD ₄	
		obs	calc ^a	obs	calc ^a
Zn	ν_1		2090.1 (73)		1488.9 (40)
	ν_2	1846.6–1821.6	1887.5 (312)	1329.8–1312.6	1345.1 (162)
	ν_3	874.2–855.2	831.6 (225)	639.9–637.5	615.2 (112)
	ν_4		325.9 (4)		311.8 (7)
	ν_5		2116.1 (156)		1527.1 (83)
	ν_6		921.0 (33)		658.5 (16)
	ν_7		486.7 (14)		364.4 (8)
	ν_8		336.6 (42)		240.6 (22)
Cd	ν_1		2088.3 (91)		1487.5 (50)
	ν_2	1745.9–1704.2	1737.9 (347)	1252.4–1224.1	1234.8 (177)
	ν_3	860.2–849.7	823.1 (276)	639.5–633.0	608.8 (139)
	ν_4		287.3 (4)		275.8 (6)
	ν_5		2116.8 (156)		1527.8 (82)
	ν_6		921.8 (36)		659.3 (17)
	ν_7		470.4 (18)		349.0 (9)
	ν_8		337.7 (41)		241.0 (21)
Hg	ν_1		2098.3 (77)		1494.2 (43)
	ν_2	1886.7–1855.9	1857.4 (478)	1354.4–1332.0	1317.0 (241)
	ν_3	871.2–860.6	827.7 (307)	647.7–643.3	612.4 (156)
	ν_4		294.7 (3)		281.6 (5)
	ν_5		2127.6 (143)		1536.2 (78)
	ν_6		920.7 (36)		658.7 (18)
	ν_7		534.8 (2)		393.6 (1)
	ν_8		364.5 (20)		260.6 (10)

^a Basis set CEP-31G, symmetry C_{3v} .

attributable to this source must be put down to a combination of the low yield, inherent low intensity, and reduced sensitivity of detection. It is possible that ν_6 contributes to the group of bands observed to develop at 930–950 cm⁻¹ irrespective of whether the metal was Zn, Cd, or Hg. However, the intensity of the bands and their preferential growth in experiments using a resonance lamp as the source of the metal vapor leaves little doubt that they arise primarily from some other product (q.v.).

The multiplet patterns characterizing the two regions of absorption we associate with ν_2 and ν_3 of the HMSiH₃ molecules cannot be ascribed wholly to simple matrix-site effects.² Apart from the primary features that we associate with well-isolated HMSiH₃ molecules, the satellites appearance typically at lower energy suggests the presence of loosely bound contact pairs HMSiH₃···X, where X is most likely to be SiH₄, M, or even H₂O impurity. Somewhat surprisingly, the relative intensities of the components in each multiplet did not appear to change appreciably when the concentration of SiH₄ was varied, or on annealing the matrix. Accordingly, it was impossible to establish with any certainty the precise origins of the individual bands. A further complication arose from the proximity of the 850–880 cm⁻¹ absorptions to a second set centered near 835 cm⁻¹. The latter normally grew in at the same rate as the first, but being much more prominent in the spectra of the deposits formed in resonance lamp experiments, it must originate in a silicon hydride product other than HMSiH₃.

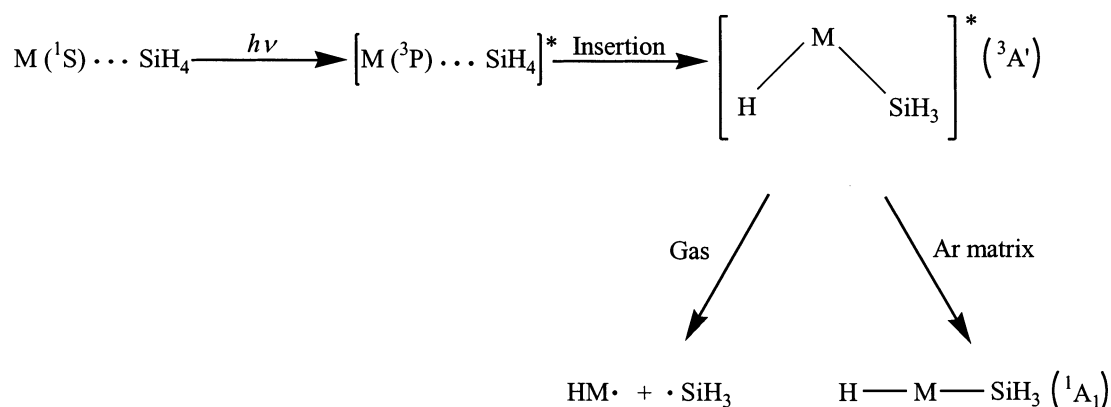
Si₂H₆. Hence two absorptions attributable to a major photoproduct have still to be positively assigned. These occur at ca. 940 and 835 cm⁻¹ with relative intensities clearly implying that they originate in the same molecule, and it is also noteworthy that the wavenumbers and profiles of the absorptions did not vary appreciably with the nature of the metal. The wavenumbers and H/D ratios afford strong circumstantial evidence that the bands represent deformation modes of an SiH_n unit. No additional features traceable to the same source could be observed in the $\nu(\text{Si-H})$ region of the spectrum, and so it must be supposed that the relevant transitions were again masked by the intense absorption hereabouts due to SiH₄.

The insensitivity to the nature of the metal clearly points to a metal-free silicon hydride. The various possibilities include the neutral molecules SiH₂, *SiH₃, Si₂H₂, Si₂H₄, and Si₂H₆. Comparison with the results of earlier matrix studies^{10,26} leads us to conclude that only one of these has the right IR credentials to be the carrier of the bands at ca. 940 and 835 cm⁻¹, namely, Si₂H₆. Thus, we find no sign of the low-wavenumber $\nu(\text{Si-H})$ absorptions characterizing SiH₂, of the symmetric $\delta(\text{SiH}_3)$ absorption at 720–730 cm⁻¹, which is the strongest feature on the spectrum of *SiH₃, or of the distinctive absorptions attributed to either Si₂H₂ or Si₂H₄.²⁶ That Si₂H₆ should be formed in our experiments need not be a matter for surprise in that it was also recognized as a significant photoproduct of earlier experiments involving matrixes doped with Hg and SiH₄.¹⁰

Matrix-isolated metal atoms are also susceptible to photoionization, especially in the presence of a suitable electron trap.^{3,30} Accordingly, we cannot altogether discount the possibility that short-wavelength UV photolysis results in electron transfer to give products of the type M⁺SiH_n⁻. Recent matrix studies of the reactions of laser-ablated Si atoms with hydrogen have led to the assignment of IR bands to the anions *SiH₂⁻ and SiH₃⁻.²⁶ Although some of our product bands appear at similar wavenumbers, they are unlikely to arise from these or other anionic species for several reasons. First, they build up on continued UV photolysis, conditions more likely to cause photodecay of such products.²⁶ Second, the bands that might be so mistaken shift markedly when the metal is changed. Finally, the H/D ratios do not support such an assignment.

HMMH. Experiments with Zn or Cd but not with Hg revealed the growth of weak bands signaling the formation of the dihydride molecules as secondary products of UV photolysis. The wavenumbers of the relevant bands are in close agreement with those reported previously for these molecules trapped in Ar matrixes.¹⁴ On the other hand, none of the experiments gave any hint of the monohydride that would be expected to absorb in the region ca. 1200–1500 cm⁻¹,^{14,15,28} nor was there anything to suggest a role for dimetal species such as HMMSiH₃, HMM, or HMMH.¹⁴ It may be noted that the dihydride is also a

SCHEME 1



secondary product that is observed to be formed when excited Zn, Cd, or Hg atoms are trapped with CH₄ in Ar matrixes.¹⁵

The only other changes in the IR spectra brought about by UV photolysis could be traced to photoinduced reactions of Zn and Cd (M) atoms with H₂O impurity, giving the insertion products HMOH.^{17,25} These could be recognized by the appearance of very weak absorptions at 1955.0 (M = Zn) and 1837.0 cm⁻¹ (M = Cd).

Reaction Mechanisms. The conditions of photolysis used in our experiments were such as to excite the group 12 metal atoms, M, trapped with SiH₄ in the Ar matrixes from their ¹S ground electronic state to the ³P excited state. The chances of populating the more energetic ¹P state were relatively slight, except when a resonance lamp was used to deliver the metal vapor to the matrix; in that case, the discharge populated both the ³P and ¹P states and generated the resonance radiation to excite other atoms. Earlier experiments and theoretical studies^{3,10,12,13} leave little doubt, it seems, that M (³P) atoms are capable of rupturing an Si–H bond of the SiH₄ molecule and that this occurs in the sequence set out in Scheme 1. Although neither the complex [M (³P)⋯SiH₄]* nor the first insertion product [HMSiH₃]* (³A') has been detected directly by experiment, the vibrational and rotational energies of •MH, one of the ultimate gaseous products, reflect the character of the transient insertion product.¹²

Evidently the initial contact pair M (¹S)⋯SiH₄ involves minimal mutual perturbation of the metal atom in its ground electronic state and the SiH₄ molecule. In this respect, SiH₄ does not differ from its less polarizable homologue CH₄.¹⁴ Only with appreciably more acidic partners, such as HCl¹⁶ and H₂O,^{17,25} is it possible to identify experimentally the formation of a distinct 1:1 adduct with the group 12 metal atom. Following excitation to its ³P excited state, the Zn, Cd, or Hg atom interacts much more strongly with SiH₄ on the evidence of theoretical calculations;^{12,13} still more significantly, insertion of the metal atom into an Si–H bond then occurs more or less spontaneously in an exothermic reaction yielding [HMSiH₃]* in its excited ³A' state. This contrasts with the behavior of CH₄ for which the corresponding reaction is calculated to be met by an appreciable activation barrier (ca. 75 kJ mol⁻¹ in the case of Zn), possibly as a result of the increased steric hindrance at the more compact and congested carbon center.^{12,13} When the reagents are isolated in a solid Ar matrix, however, the outcome is the same for CH₄ and SiH₄, with HMEH₃ (E = C or Si; M = Zn, Cd, or Hg) having a linear H–M–E skeleton in its ¹A₁ ground state being identified as the primary product. The conflict between experiment and theory in the cases where M = Zn or Cd and E = C cannot be easily resolved; it may be that the M (³P)⋯CH₄ complex absorbs a second photon to reach a higher

TABLE 7: $\nu(\text{M}-\text{H})$ Wavenumbers (in cm⁻¹) for HMX Molecules Isolated in Ar Matrixes

molecule	M = Zn	M = Cd	M = Hg	ref
HMH	1870.2 ^a	1753.5 ^a	1943.7 ^{a,b}	14, 28
HMCl	1952.3	1835.8	2092.0	16
HMOH	1955.0	1837.0	2116.5	17, 25
HMCH ₃	1866.1	1760.5	1955.3	15
HMSiH ₃	1846.6	1745.9	1886.7	this work

^a Antisymmetric $\nu(\text{M}-\text{H})$ mode. ^b N₂ matrix.

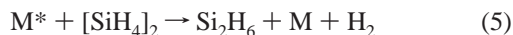
excited state with energy sufficient to overcome the barrier to insertion. No such conflict exists for the reactions of M (³P) with SiH₄, although this does not mean of course that the possibility of two-photon processes is to be excluded.

In the gas phase, the initial insertion product [HMSiH₃]* (³A') undergoes fragmentation with the formation of the radicals •MH and •SiH₃ (reaction 2). It may be that fragmentation also occurs when the reagents are held in a solid Ar matrix but that the failure of either fragment to escape from the matrix cage results in recombination to produce HMSiH₃ in its ¹A₁ ground electronic state; thermodynamically, this is the best favored of all the possible outcomes short of returning to M (¹S) + SiH₄. Unfortunately, our experiments give no clue to whether this or physical relaxation of the [HMSiH₃]* (³A') molecule, made possible by spin–orbit coupling and/or matrix mediation, is the principal agency leading to the observed insertion product. The IR spectra of the photolyzed matrixes certainly gave no signs suggesting the presence of either •MH^{14,15,28} or •SiH₃²⁶ radicals. Traces of the dihydrides HMH¹⁴ were observed in our experiments with M = Zn or Cd but not with Hg. These may be formed from traces of H₂ impurity in the matrix, or they may be the outcome of secondary changes. For example, reaction 3 would give rise to H• atoms, which are known to be quite mobile in Ar matrixes³⁰ and could compete with •SiH₃ to trap a fraction of the •MH radicals. Alternatively, reaction 4 would deliver the dihydride directly, but of the expected coproduct SiH₂,²⁶ we could find no trace.

With only two vibrational fundamentals that can be characterized in practice, the HMSiH₃ molecules do not lend themselves to detailed vibrational analysis. We note, however, that the $\nu(\text{M}-\text{H})$ modes occur at wavenumbers wholly in keeping with those of related molecules (see Table 7). The two regions of absorption associated with HMSiH₃ displayed relatively rich multiplet patterns that must be attributed to the occupation of different matrix sites, including some which incorporate species other than Ar and so give rise to loosely bound contact pairs of the form HMSiH₃⋯X, where X = SiH₄, M, or trace impurities such as H₂O. All of the relevant features grow on continued photolysis. That some do this at a faster rate than others (q.v.)

may be a sign of secondary reactions, but equally well it may reflect merely the known phenomenon³¹ of varying photosensitivity from one matrix site to another. The multiplets, which were also observed in the earlier study of the Hg/SiH₄ system,¹⁰ are consistent with a mechanism involving the breakup of the initial insertion product [HMSiH₃]* (³A') followed by recombination of the HM• and •SiH₃ radicals within the confines of the matrix cage. The various components then reflect changes of orientation of the product molecule as well as differences in the character of the matrix cage.

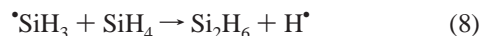
One of the most puzzling features of this and the earlier¹⁰ study is the provenance of Si₂H₆, which is the only other photoproduct to appear in all experiments in concentrations comparable with that of HMSiH₃. Si₂H₆ is formed when matrix-isolated SiH₄ dimers are irradiated with far-UV light (λ = 193 nm),¹⁰ but this two-photon process is unlikely to contribute significantly to the yield of Si₂H₆ observed in the experiments with group 12 metal atoms. Instead, Legay-Sommaire and Legay have suggested¹⁰ that the excited metal atoms act on adjacent SiH₄ dimers to promote reaction 5; the dihydride HMMH may then be a secondary product as excited metal atoms compete for the H₂ thus formed.^{14,28} Alternatively HMSiH₃ may be



photoinduced to react with a neighboring SiH₄ molecule in accordance with eq 6. Support for the second mechanism was provided in the earlier Hg/SiH₄ experiments¹⁰ by the finding that prolonged irradiation caused a decrease in the intensity of



the IR absorptions attributed to HHgSiH₃⋯SiH₄ contact pairs. No such decrease was observed in our experiments, but the intensities of the main low-wavenumber satellites, most plausibly identified with HMSiH₃⋯SiH₄ pairs, did grow distinctly more slowly than the features associated with HMSiH₃ surrounded exclusively by Ar atoms. A further possibility, not considered previously, is that trapping of the HM• and •SiH₃ radicals formed by fragmentation of the ³A' insertion product does not lead exclusively to HMSiH₃ (¹A₁), but that reaction of the fragments with SiH₄ contained in some of the matrix cages leads to the reactions 7 and 8



A surprising feature of our results is that the relative yields of HMSiH₃ and Si₂H₆ did not vary appreciably with the concentration of SiH₄ in the matrix, although the degree of photoconversion was invariably small. It is difficult therefore to reconcile this result with reactions that require only one SiH₄ molecule (to form HMSiH₃ by reaction 1) and two SiH₄ molecules (to form Si₂H₆, whether by reaction 5 or 6). It seems altogether more likely that reactions 7 and 8 are actually the primary sources of the two main products observed in our experiments with thermally generated metal atoms. The need for the intervention of two further SiH₄ molecules to form either HMSiH₃ or Si₂H₆ would then account not only for the near invariance of the relative yields with concentration but also for the paucity of these yields. On this basis, it must be supposed that, without an SiH₄ molecule in the matrix cage, the triplet insertion product reverts to M (¹S)⋯SiH₄.

When the group 12 metal atoms are introduced from a resonance lamp, reaction with SiH₄ occurs during co-deposition but with Si₂H₆ now as the dominant product. It is difficult to know in these circumstances the parts played by metal atoms in the more highly excited ¹P state and by the greater mobility enjoyed by reagents and products alike during condensation. The conditions come closer to those prevailing in the gas phase where •SiH₃ formation becomes a major reaction channel in the metal-sensitized decomposition of SiH₄; the energy content of the reaction channel may then be such as to dissociate the weakly bound •MH radical.¹⁰ Dimerization of the •SiH₃ radicals during deposition would then account for the formation of Si₂H₆; alternatively, reaction 5 may become important at the deposition stage.

Our experiments give no reason to believe that well-isolated HMSiH₃ molecules differ from the HMCH₃ molecules,¹⁴ which are photostable under the conditions of broad-band photolysis used to generate them. There is no hint of decomposition to form either •MH or •MSiH₃, matching the behavior of HAlSiH₃ and HGaSiH₃ in similar conditions, nor is there any definite sign that insertion can be reversed, although this would actually be difficult to establish when photoconversion is relatively inefficient and in the absence of any distinctive mark of the precursor, i.e., the M (¹S)⋯SiH₄ contact pair.

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