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Photochemical Insertion Reaction of Hg in SiH_4/SiD_4 in Low-Temperature N_2, Ar, and Kr Matrixes. Formation of Radicals in Kr

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The products of the insertion reaction of Hg($^3P_1$) in the SiH (SiD) bond of *h*- or *d*-silane in nitrogen and rare gas matrixes are observed by FTIR spectroscopy. This study has shown that the reaction takes place without activation energy. Disilane molecules are formed from the dimers of parent molecules close to mercury or from the complexes of the insertion products with the parent molecules. In this last case a weak isotopic effect shows that the reaction probably takes place through a small barrier. In the krypton matrix the formation of SiH_2 and SiH radicals is observed by a mercury-sensitized two-photon excitation. The SiH_3 radical is produced upon annealing. A mixed CH_4/SiH_4 experiment gives the ratio of the insertion rates in these two molecules.

1. Introduction

The reactivity of metal atoms with hydrogenic molecules has been largely studied in the past, a recent review is available in ref 1. Perutz[2] gave in 1985 an exhaustive review of the photochemical reactions involving atoms isolated in matrixes. Since that time, many experiments have been done because these reactions play an important role in different fields of research. A theoretical study of the mercury-sensitized reactions has been done by Siegbahn et al.[3] who explain that the reactivity of Hg and silane is due to the low value (90 kcal/mol) of the Si−H bond strength compared to that of the C−H bond strength in CH_4. Our aim in studying the reaction of Hg($^3P_1$) with molecules isolated in matrixes is to get a better understanding of the barrier to reaction and to trap some new species that may play a role in the chemistry in gas phase as intermediates in the reactions.

In a previous study of the reaction of Hg with H_2[4] and CH_4,[5] we showed the formation of the insertion products HgH_2 and $HHgCH_3$ and the corresponding deuterated species. In the case of methane, a strong kinetic isotopic effect was found between CD_4 and CH_4, the reaction being much more efficient with CH_4. This means that there is a small barrier to the insertion when Hg is excited in the low-temperature solid at 249 nm, i.e., 825 cm^{-1} higher in energy than Hg($^3P_1$) in the gas phase.

As Breckenridge[1] has predicted that the insertion reaction must be much easier in the Si−H bond than in the C−H bond, we have undertaken this new series of experiments on the SiH_4 and SiD_4 molecules. The initial steps of the reactions in the solid and gas phases are not very different, and the main interest in the solid is that some unstable species may be stabilized giving a better understanding of the gas-phase reaction.

The IR spectra of matrix-isolated SiH_4 and SiD_4 have been studied in rare gases and nitrogen matrixes.[6] These spectra show that the silane molecule occupies two different sites in the matrix. Allen and Schaeffer[7] give an important theoretical paper, including an extensive review of experimental works, on the structure, force constants, and vibrational spectra of SiH_4 and the SiH_3, SiH_2, and SiH radicals.

The VUV photolysis of silane in an argon matrix was first achieved by Milligan and Jacox,[8] who observed the formation of Si_2, SiH_2, SiH, and SiH_3. The assignment of some IR absorption bands to the radicals SiH_2 and SiH_3 has been discussed and modified by Fredin et al.[9] These authors have studied the reaction of Si atoms with H_2 in the gas phase, and trapped the products in argon matrixes. They assigned the lines observed to SiH_2, but found frequencies different from those assigned to SiH_2 by Milligan and Jacox.[8] They concluded that one should exchange the assignment of Milligan and Jacox[8] for SiH_2 and SiH_3, without observing SiH_3 themselves. This new assignment was accepted by Abouaf-Marguin et al.[10] who trapped the radicals produced in a silane plasma discharge, and also afterward by Jacox.[11] No previous data exist in krypton matrixes.

2. Experiments

The experimental setup has been described previously.[4] It consists mainly of a cold cubic copper cell with a CsBr window on one face and on the opposite face a PTFE cover with a 6 mm hole to introduce the deposition tubing. The cell is at the cold end of a liquid helium cryostat. The cryostat may be turned so that the sample may be perpendicular to the deposition tubing or to the optical axis of the FTIR Bruker IFS 120 spectrometer or to the light beam for the excitation of mercury.

SiH_4 (Messer France ultrahigh purity $\simeq$ 99.99%) or SiD_4 (Cambridge Isotope Laboratory 98% -d_4), or a mixture of the two, premixed with nitrogen (Air Liquide 99.9999%), argon (Messer France 99.9999%), or krypton (Messer France 99.99%) is sent through a Granville−Phillips needle valve and then through a sintered steel filter (15μm) containing a drop of mercury. We take care not to have too many mercury dimers. The concentration of mercury is changed, but not measured, by adjusting the gas flow. From previous experiments we know that the maximum mercury content is 10^{-3}. The highest concentration of mercury is achieved with the lowest flow

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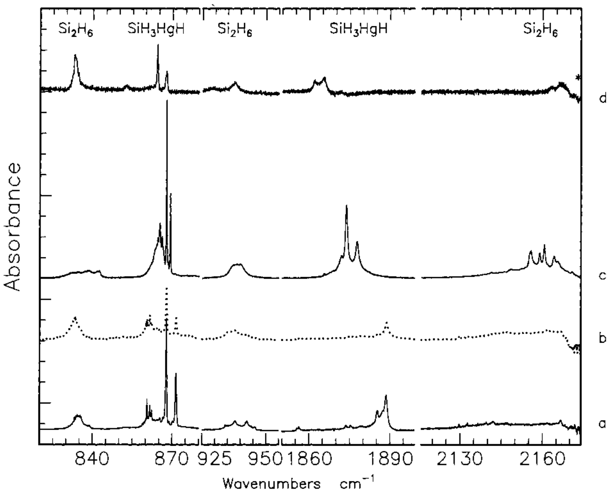

Figure 1. Hg/SiH_4/Ar; 6.4 mmol deposit: SiH_4/Ar: 0.9/1000 after 4000 KrF (9 mJ) pulses (a); SiH_4/Ar: 1.5/1000 after 90 min deuterium lamp irradiation (b); Hg/SiH_4/N_2: 1.4:1000, 6.2 mmol deposit, after 1500 KrF (11 mJ) pulses (c); Hg/SiH_4/Kr: 1:1000, 6.2 mmol deposit, after 2600 KrF (9mJ) pulses (d). The spectrum of radicals is shown in other figures.

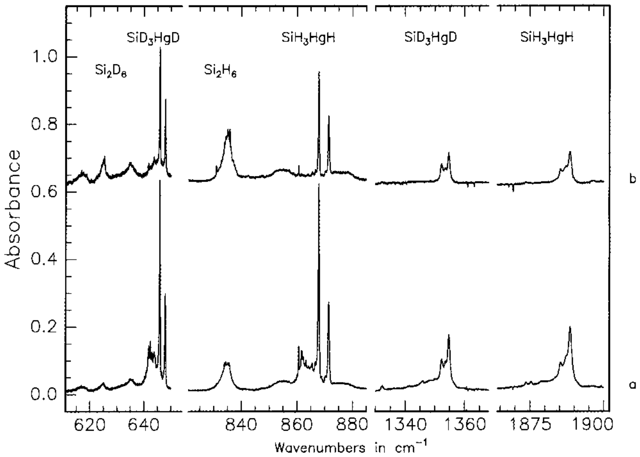

Figure 2. Hg/SiH_4/SiD_4/Ar 2.3:2.3:1000, 6.2 mmol deposit, after KrF (11 mJ) irradiation, 200 pulses (a); 11 700 pulses (b).

TABLE 1: Wavenumbers of the Absorption of the Stable Products in cm^{-1} (measured after annealing)

Ar matrix	Kr matrix	N_2 matrix	assignment
833.56	831.6	833.7	Si_2H_6
833.77	833.10	836.65	Si_2H_6
834.6	833.85	838.4	Si_2H_6
		841.7	Si_2H_6
		842.5	Si_2H_6
858−866		860−867	$SiH_3HgH\cdots P$
867.80	864.36	867.84	SiH_3HgH
871.42	867.41	869.26	SiH_3HgH
	867.83		SiH_3HgH
938	936.9	938	Si_2H_6
		1743.5 w[a]	SiNN
		1754.8 m[b]	SiNN
		1761.5 w[a]	SiNN
		1774.9 w[a]	SiNN
1885.25	1861.92	1872	SiH_3HgH
1887.22	1863.25	1873.74	SiH_3HgH
1888.49	1865.42	1877.67	SiH_3HgH

[a] w: weak. [b] m: medium.

TABLE 2: Wavenumbers of the Absorption of the Stable Deuterated Products in cm^{-1} (measured after annealing)

Ar matrix	Kr matrix	N_2 matrix	assignment
616.4	616.3		Si_2D_6
616.68			$Si_2\ D_6$
619.38			Si_2D_6
642.5	641.2	644	SiD_3HgD
645.91	643.18	646.54	SiD_3HgD
647.94	645.02	647.10	SiD_3HgD
679	677.9		Si_2H_6
1352.23	1336.1	1343.2 sh[a]	SiD_3HgD
1353.58	1336.9	1344.4	SiD_3HgD
1354.70	1338.2	1344.9	SiD_3HgD

used: 0.15 mmole/min. The deposition temperature is 25 K, and the spectra are recorded at 6 K, with 0.1 cm^{-1} resolution.

The excitation of mercury atoms is provided either by a deuterium lamp or by a SOPRA KrF excimer laser, generally unfocused, giving energy up to 16 mJ on a ≅1 cm^2 joulemeter placed in front of the sample at 25 cm. The intensities given for the laser are only good for relative comparison of one experiment to another and not for absolute values. Crépin and Tramer[12] found that the UV absorption of mercury atoms trapped in a silane matrix decreased with time under the irradiation by the deuterium lamp used as a source. It is why we have used such a lamp for some of the photochemistry experiments. The advantage, for one-photon processes, compared to the laser excitation is that the irradiation conditions are very reproducible; the disadvantage is that much longer irradiation times are needed to get the same amount of insertion product and consequently fewer experiments can be done on the same sample. The spectra of the products are detected by FTIR spectroscopy. The spectrum before irradiation is taken as a reference so that the spectra shown in the figures are difference spectra; only the products show positive absorbance.

3. Results and Discussion

3.1. Insertion Products: SiH_3HgH. Mercury atoms embedded in rare gases and nitrogen matrixes show Hg($^3P_1 \leftarrow {}^1S_0$) absorption at 249 and 246.5 nm for N_2, 246 nm for Ar, and 249.5 nm for Kr.[13] In the present experiments a mercury atom is excited in the $^3P_1$ state (Hg*), and it then reacts with a silane molecule close to it, if there is any.

The spectra of the products obtain by irradiation of two SiH_4/Ar samples, one by the KrF laser (Figure 1a) and the other by the deuterium lamp (Figure 1b), show that the main products of the reaction (Hg($^3P_1$) + SiH_4) are the same. The same products are also obtained in nitrogen and krypton matrixes (Figure 1 c,d), however, with variable proportions of the different species.

The spectrum of the products obtained for a SiD_4/SiH_4/Hg/Ar matrix (Figure 2) shows the effect of isotopic substitution. The new absorption bands are easily assigned to $HHgSiH_3$ and $DHgSiD_3$ by comparison with previous experiments in methane and hydrogen where the Hg−H stretching frequency is characteristic in the 1850−1950 cm^{-1} region and Hg−D in the 1350−1420 cm $^{-1}$ region. Si_2H_6 and Si_2D_6 bands are also observed. The frequencies of the *h*- and *d*-products are shown respectively in Tables 1 and 2. The wavenumbers for the deuterated species are less accurate because the experiments have been done with mixed samples containing half *h*- and *d*-compounds and consequently the lines are broader due to the variety of neighbors.

Doubling the laser intensity increases by a factor less than two the absorption of the insertion molecule, showing that the insertion reaction needs only one laser photon. Comparing the relative intensities of the $HHgSiH_3$ and $DHgSiD_3$ obtained on mixed samples containing half SiH_4 and half SiD_4 (see Figure 2), and taking into account that the intensities are proportional

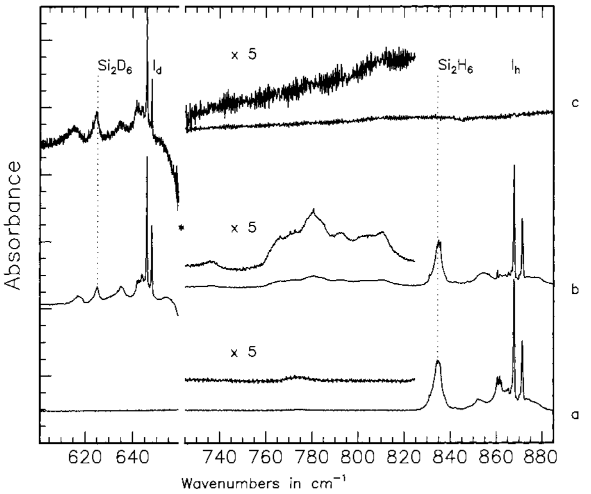

Figure 3. Spectra after KrF laser irradiation, 6.2 mmol deposit, from 730 to 820 cm^{-1} top traces amplified by 5. $Hg/SiH_4/Ar$ 2.6:1000, 6000 pulses (10 mJ) (a); $Hg/SiH_4/SiD_4/Ar$ 2.3:2.3:1000, 1500 pulses (11 mJ) (b); $Hg/SiD_4/Ar$ 2.6:1000, 3200 pulses (9 mJ) (c). $I_h = SiH_3HgH$, $I_d = SiD_3HgD$, * = SiD_4.

to the frequencies under H → D substitution, one finds the same amount of product with the SiH_4 and SiD_4 molecules, within the experimental error limits (≈5%). This clearly means that, contrary to the insertion of Hg* in methane, there is no potential barrier to Hg* insertion in silane, confirming the theoretical expectation.[1,3]

It should be noted that the insertion products in Ar matrixes appear from the very beginning of the irradiation; with the lamp, their concentration keeps growing for more than 1 h. At low concentration (1/1000), it is the same under mild KrF irradiation.

At a high enough concentration (0.23%) and with the KrF laser gently focalized (10 mJ), the maximum intensity is obtained in a few minutes (Figure 2a). If the irradiation is continued, the amount of insertion product decreases (Figure 2b) and more Si_2H_6 is formed. We assign to complexes of SiH_3HgH (SiD_3HgD) with SiH_4 or SiD_4 the absorption observed on the low-frequency side of the main band, lying at 860−865 cm^{-1} for the SiH_3HgH complexes and 640−645 cm^{-1} for the SiD_3HgD complexes (Figure 2a). These bands decrease under longer irradiation time (Figure 2b) and are probably partly responsible for the simultaneous growing of the disilane absorption. The details observed are shown for three different matrixes: $SiH_4/Hg/Ar$ (Figure 3a), $SiH_4/SiD_4/Hg/Ar$ (Figure 3b), and $SiD_4/Hg/Ar$ (Figure 3c). In the case of the mixed matrix (Figure 3b), a flat broad absorption band between 750 and 820 cm^{-1} is observed which may be due to various *h*- and *d*-disilanes. However, we shall notice (Figure 3b, Figure 2) that, even with a sample containing the same amount of SiH_4 and SiD_4, providing exactly the same conditions of irradiation, SiH_3HgH is more efficiently dissociated than SiD_3HgD, and more Si_2H_6 than Si_2D_6 is formed. This may be an indication that there is a small barrier to the dissociation of $HHgSiH_3$ which gives different yields under H−D substitution.

In the nitrogen matrix the $HHgSiH_3$ molecule does not dissociate under prolonged irradiation, the matrix is more rigid, and the barrier is perhaps more difficult to overcome.

3.2. Si_2H_6. Some lines easily assigned to Si_2H_6, are observed. The IR spectra of disilane are known,[14] and Si_2H_6 has been observed in the VUV photodissociation of silane.[9] We have also produced Si_2H_6 by UV excitation at 193 nm of highly concentrated silane samples without mercury. In the Kr matrix, Si_2H_6 is formed upon irradiation of SiH_4 dimers, without mercury, at 249 nm, but in much smaller quantities. These reactions are induced by the two-photon absorption.

The mechanism of thermal decomposition of silane has been investigated in the gas phase by Neudorf et al.[15] They find that the main channel is the following:

$$SiH_4 \rightarrow SiH_2 + H_2 \tag{1}$$

with an activation energy of 55 kcal/mol and

$$SiH_2 + SiH_4 \rightarrow Si_2H^*_6 \tag{2}$$

with almost the same activation energy: 54.8 kcal/mol. In the gas phase, this last reaction is responsible for the formation of disilane with a high internal energy content (49 kcal/mol[16]). From the standard enthalpy of formation of SiH_4 and Si_2H_6[17] one finds

$$2\ SiH_4 \rightarrow Si_2H_6 + H_2 - 2.8\ \text{kcal/mol}$$

The electronic energy content of Hg* is about 114.8 kcal/mol, thus:

$$Hg^* + 2\ SiH_4 \rightarrow Si_2H_6 + H_2 + Hg + 112\ \text{kcal/mol} \tag{3}$$

The energy of the reaction is sufficient to overcome the barriers to reactions 1 and 2, and explains the one-photon formation of Si_2H_6. The energy content of the reaction is even sufficient to produce H atoms instead of H_2 molecules. However, Chantranupong et al.[18] predict theoretically an activation energy of 108.25 kcal/mol for reaction 1; in this case only H_2 molecules and not H atoms may be produced. As we are not able to detect H atoms, it is impossible to say whether the experimental or theoretical activation energy is the better one.

It should be noticed that, in the gas phase, the SiH_3 + H channel for the decomposition of silane is a minor one compared to reaction 1,[15] with an interesting exception for the mercury-sensitized reactions[19] where SiH_3 formation is observed. A tentative experiment[20] to observe HgH formation in the Hg* + SiH_4 reaction in a molecular jet has failed, showing that the energy content of the reaction does not allow the stabilization of the HgH molecule observed in similar conditions in the Hg + H_2 reaction. Our experiments show that in the solid phase the SiH_3 + H channel is replaced by the insertion mechanism.

It seems reasonable to assume that the formation of the disilane molecules in our experiments proceeds either by reaction 3 from the silane dimers close to mercury or through the following reaction involving the SiH_3HgH formed in first neighbor of a silane molecule:

$$SiH_4 + SiH_3HgH + h\nu_{249} \rightarrow Si_2H_6 + Hg + H_2 \tag{4}$$

This reaction can explain the intensity decrease of the SiH_4−SiH_3HgH complex (molecules in first neighbor position) under prolonged irradiation in the argon matrixes. As the Hg atoms are well isolated, very few insertion products are likely to be close to an Hg atom, so that in this reaction the molecule SiH_3HgH is the one which absorbs the laser photon (249 nm). It explains also why the SiH_3HgH may be dissociated by prolonged irradiation.

We supposed that HgH_2 might be an intermediate in reaction 4, but we do not see the absorption of this already known molecule—the excess of energy available probably produces the dissociation. The dissociation energy of HgH_2 has been evaluated at about 69 kcal/mol.[21] However in the nitrogen matrix, we observe very weak absorption at 1943 and 781 cm^{-1},

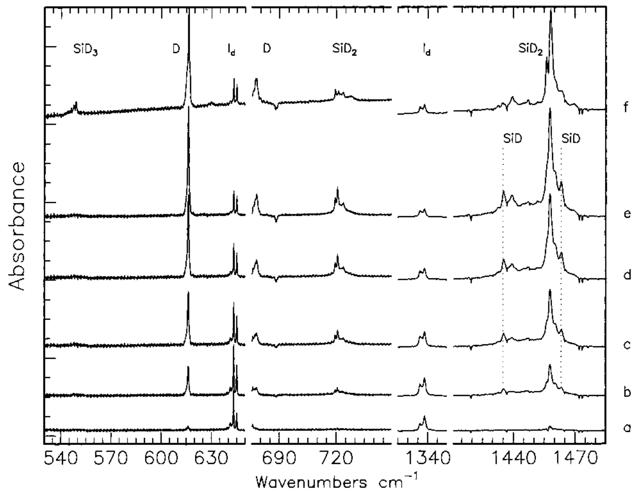

Figure 4. $Hg/SiD_4/Kr$: 2:1000, 4.7 mmol deposit, at increasing irradiation by KrF laser (4 mJ), 100 pulses (a); 600 pulses (b); 1600 pulses (c); 3600 pulses (d); 6600 pulses (e), after annealing at 32 K (f). $I_d = SiD_3HgD$, $D = Si_2D_6$.

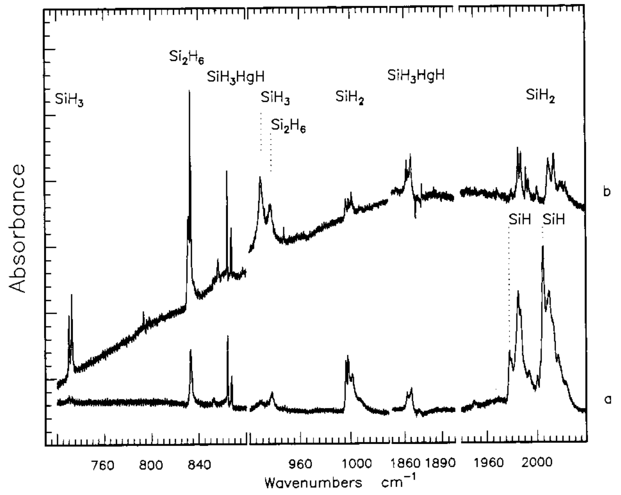

Figure 5. $Hg/SiH_4/Kr$, 1:1000, 6.2 mmol deposit, after 2600 KrF laser pulses (9 mJ): before annealing (a), after 15 min annealing at 35 K (b).

assigned to HgH_2, but this occurs only in a few experiments where the KrF was very powerful (>12mJ), the only experiments where the absorption of the insertion product decreases after prolonged irradiation.

In the nitrogen matrix we observe also a weak sharp band at 1754.8 cm^{-1} in a group of very small features that may be assigned to SiN_2,[22] showing the presence of Si atoms.

3.3. Production of Radicals in Kr Matrixes. In the case of the krypton matrixes, under experimental conditions similar to that in argon, and by KrF laser irradiation of a few mJ energy, we observed less insertion product than in argon (Figure 1), but some radicals (SiH and SiH_2) appear (Figures 4 and 5) that we were never able to obtain with the deuterium lamp as a source, or with the KrF laser at 0.6 mJ energy (5 to 20 times less than usual).

To try to understand the different mechanisms involved in these reactions, we have done the following: (i) irradiation with the deuterium lamp for 50 min, during which the intensity of absorption of SiH_3HgH reached a plateau; (ii) a further irradiation for 90 min to ensure that we could not get more product; (iii) then irradiation by KrF laser (2 mJ) 500 pulses. We expected that after steps (i) and (ii) all the Hg atoms close to a silane molecule will be inserted, but step (iii) shows an increase of the insertion products together with the appearance of the radicals.

TABLE 3: Wavenumbers of the Absorption of the Radicals in Kr Matrix (cm^{-1})

before annealing
  SiH: 1977.83 2004.75
  SiD: 1435 1463
after annealing
  SiH_3: 730.01 732.45 929
  SiD_3: 547.2 548.9
  SiH_2: ν_2: 996.34 998.53 1000.96
    ν_3, ν_1, $2\nu_2$ 1st site: 1985.4 1987.6 1991.6 1993.7 2000.3
      2nd site: 2009.4 2013.8 2022
  SiD_2: ν_2: 721
    ν_3, ν_1, $2\nu_2$ 1st site: 1439 1447 1456.3
      2nd site: 1457.7 1460.4

It means that there is an equilibrium between the insertion reaction giving SiH_3HgH, and the dissociation of this molecule. We have also verified that the equilibrium value depends on the intensity of the light, even with the deuterium lamp, different focalization gives different values of the “plateau” without formation of radicals. In a given sample containing both SiH_4 and SiD_4, the production of SiH_3HgH and SiD_3HgD is proportional to the initial concentration of the parent molecules. It is the same for the radicals, but the proportion of radicals obtained relative to the concentration of the parents varies very much from one experiment to another following the KrF laser energy. When the intensity of the laser is multiplied by two, going from 2 to 4 mJ, the intensity of the radical is multiplied by four showing a two-photon absorption process. However, when the intensity is multiplied by 4, going from 4 to 16 mJ, the intensity of the radicals is only multiplied by 6, showing a saturation of the two-photon absorption. It should be noted that the intensity measurements of the laser are only mean values, the intensity being far from constant from one pulse to another.

3.3.1. The Silylene Radical: SiH_2. Before annealing, two radicals are observed: SiH_2 and SiH (see next section). SiH_2 has been observed previously[8−10] in argon matrixes, with main absorption bands in the 2000 and 1000 cm^{-1} regions (1460 and 720 cm^{-1} for SiD_2). We must note that the spectra observed in the 2000 cm^{-1} region have multicomponent structures very similar to those observed in the argon matrixes,[8−10] but shifted. In agreement with Fredin,[9] we assign the lines pertaining to the SiH_2 absorption by the correlation of the line intensities in the two regions. This has been done with a very large number of spectra obtained in various conditions of concentration, temperature, and thermal history (e.g., annealing at different temperatures). The frequencies are shown in Table 3. However for argon matrixes, the assignments have been done by Fredin et al.[9]—ν_2 around 1000 cm^{-1}, ν_1, ν_3, and $2\nu_2$ at increasing frequencies in the 2000 cm^{-1} region. The IR frequencies for ν_1 and ν_3 are so close that we do not think it is possible to propose a vibrational assignment. Two groups of SiH_2 bands are observed, the distance of which is almost the same as that of the two groups of SiH_4 absorption in Kr corresponding to the occupation of one or two sites.

Comparing our results in Kr matrixes with those of Milligan and Jacox[8] and of Fredin et al.[9] in Ar matrixes, it appears that (i) Fredin et al. observe only SiH_2, (ii) Milligan and Jacox observe the same lines as Fredin (1967, 1974, and 1993 cm^{-1}) together with another group of lines, as we do. We think that apart from the lines at 1955 and 1999 cm^{-1} in Ar,[8] which may be assigned to SiH (see next section), the whole absorption recorded in the 2000 cm^{-1} range is due to SiH_2 in different sites and not to SiH_3, as it will be proved in the next section. This conclusion is further supported by the comparison with the spectra of the parent molecule in Ar and Kr matrixes; as mentioned previously the SiH_4 molecule shows two absorption bands around 2200 cm^{-1}, the highest frequency one being more intense in Kr and the lowest frequency one in Ar. It is remarkable that the distance between the two groups of SiH_2 bands in ref 8 is almost the same as the distance between the two absorption bands of silane in Ar, and the same result is obtained here in Kr. It is clearly seen in the Fredin spectrum (ref 9, Figure 1) that the second (higher frequency) site is also present, but only one weak line around 2020 is seen, it corresponds to the most intense line of the other site lying at 1973.3 cm^{-1}. The main difference between the two experiments[8,9] is that in the latter, the SiH_2 molecule is made in the gas phase and then deposited in an argon matrix in contrast to the former one where the radicals are made in situ and have a different environment, the same as here in Kr.

Figure 4 clearly shows that under strong KrF laser irradiation the intensity of the insertion product SiD_3HgD increases (Figure 4a,b) and then decreases (Figure 4c,d,e), whereas the SiD_2 absorption increases throughout the irradiation time and decreases only upon annealing. Si_2D_6 also increases under irradiation.

3.3.2. SiH_3, SiH. Some of the products absorbing in the 2000 cm^{-1} region have no counterpart in the 1000 cm^{-1} region. Furthermore, the lines observed at 1977.8 and 2004.7 cm^{-1} before annealing are not correlated in intensity through the whole spectrum (from 530 to 4000 cm^{-1}). Some authors[8−10] have assigned some lines in the 2000 cm^{-1} region to SiH_3. In agreement with Allen et al.,[7] our experiments show that it is not the case here, because one of the SiH_3 bands, the doublet around 730 cm^{-1} that has been well studied by different methods,[23,24] is not correlated with these bands. In our experiments, the appearance upon annealing of the SiH_3 doublet at 730 cm^{-1} correlates with the decrease of the $\approx$2000 cm^{-1} bands. Furthermore, we observe that this 730 cm^{-1} band decreases upon further KrF irradiation. This shows that the SiH_3 radical absorbs the laser light[25] and dissociates in agreement with the early theoretical work of Olbrich,[26] who found that the first excited state of SiH_3 is a Rydberg state at 41 900 cm^{-1} dissociating into $SiH_2 + H$.

Annealing at 32 K, instead of 35 K, gives a slightly different silylene radical absorption, with the same overall intensity in the ν_2 region (720 cm^{-1} for SiD_2). In the other region (ν_1, ν_3) where SiD may be found together with SiD_2, only the SiD lines at 1435.5 and 1463 cm^{-1} decrease at the same time as SiD_3 is increasing. The corresponding lines for SiH are at 1977.8 and 2004.8 cm^{-1}. These lines attributed to SiH (SiD) grow faster at the beginning of the irradiation than those attributed to SiH_2 (SiD_2), and it is also a way to distinguish between them.

The appearance upon annealing ($T > 31$ K) of the SiH_3 absorption may be due to migration of H or H_2 and recombination with SiH_2 or SiH, respectively; this may explain the correlated decrease of the bands in the 2000 cm^{-1} region. The only lines which decrease to null absorption under annealing are the SiH lines, so we think that the mechanism is probably $SiH + H_2 \rightarrow SiH_3$ and $SiH_2 + H_2 \rightarrow SiH_4$, the H atoms recombine probably fastest just after the dissociation.

3.3.3. ArF Laser Irradiation. ArF laser (193 nm) irradiation of a 7/1000 SiH_4/Kr sample without Hg produces essentially Si_2H_6 (833.7 and 937.4 cm^{-1}) but also some species absorbing only at 1977.5 cm^{-1}, which disappears upon annealing at 35 K and that can be assigned to SiH.[27−29] Furthermore, as SiH disappears under annealing, an absorption appears as a sharp doublet at 730 and 732.5 cm^{-1} together with a broader band at 929 cm^{-1} which corresponds to SiH_3 absorption well-known in the literature by its characteristic doublet at 721 and 727.9 cm^{-1} in the gas phase.[23] The assignment of the 929 cm^{-1} line in Kr matrix and the 925 cm^{-1} line in Ar[8] to the ν_4 vibration fits well with the prediction of Allen et al.[7] As it has been predicted by Allen,[7] the vibrations ν_1 and ν_3 are too close to those of the parent molecule to be observed here.

To conclude, we think that in addition to the SiH_2 radical, the absorption bands observed in the 1950−2000 cm^{-1} region are due to SiH. One of them (1978 cm^{-1}) corresponds fairly well to a frequency assigned, in the gas phase, to this SiH radical.[27,28] As for SiH_2, we observe two sites for SiH which corresponds to radicals formed from the reaction with SiH_4 in its two different sites (replacing one or two Kr atoms). We also think that under annealing the migration of the hydrogen produces SiH_3.

It should be said that the UV photodissociation of dimethyl mercury in argon matrixes,[30] gives $C_2 H_6$ disturbed by Hg atoms in various positions, and the spectrum of $C_2 H_6$ is much more complicated than the one directly obtained for a C_2H_6/argon matrix. Therefore we assume that the spectrum of SiH and SiH_2 radicals may be more complicated when the radicals are formed in situ than when prepared in gas phase and deposited afterward.

We can conclude also that a spectrum which does not show a band in the 730 cm^{-1} region cannot be assigned to SiH_3, because this line is the most intense absorption of the SiH_3 radical outside the absorption range of the parent molecule.

By ESR spectroscopy, Nakamura et al.[31] have identified SiH_3 and SiH_5 as the radicals produced in Kr and Xe matrixes by reaction of H atoms with silane, the SiH_5 radical being an intermediate in the formation of the silyl radical. We have not found any line that we can assign to SiH_5 in these experiments, perhaps because we do not produce enough H atoms or because they recombine into H_2 before reaching a silane molecule.

It should be noted that after irradiation of the dilute mixed samples SiH_4/SiD_4/Kr, no mixed products such as SiHD are observed, in agreement with the fact that the silylene radical is produced by the dissociation of a monomeric species. After annealing, the *h*-and *d*-silylene intensities decrease, but the SiH_3 and SiD_3 absorption observed in mixed *h*- and *d*-silane matrixes have much smaller intensities than in pure *h*- or *d*-samples of the same concentration, probably because of mixed H- and D-recombination. Therefore the mixed samples, after annealing, show too small intensities for the silyl radical and we were not able to find the absorption lines of SiH_2D and $SiHD_2$. As a matter of fact, it is difficult to increase the concentration of silane in the matrix because it increases the concentration of aggregates, and not that of isolated molecules. The best samples have been obtained with less than 3/1000 each of *h*- and *d*-silane.

It should be noted that, after irradiation, the hydrogen atoms or molecule stay close to the radical produced at the same time, therefore it is easier for them to recombine with this radical than with other ones which are far away at this low concentration, it is the reason the mixed radicals show very small absorption.

3.4. What is the Mechanism of Formation of the Radicals, and Why in Kr and not in Ar matrixes? A clear point is that the formation of the radicals needs two KrF laser photons and mercury atoms. Without mercury we observed only the formation of disilane, except with ArF laser (193 nm) where SiH is also obtained. Furthermore it is known from a molecular beam experiment[32] that silane absorbs at 125.1 nm giving Si atoms and SiH radical (but no SiH_2 or SiH_3), this wavelength corresponds to exactly twice the energy of the KrF laser. Therefore we suppose that the SiH radical is obtained directly from a two photon excitation of the SiH_4 molecule involved in a van der Waals complex with Hg, Hg playing the role of the intermediate state to provide the two photon absorption. Furthermore this same reaction which in the gas phase gives Si atoms and SiH radicals must also give hydrogen, which can recombine in matrixes to give the SiH_2 or SiH_3 radicals. As we have seen previously, the last one is destroyed by KrF laser irradiation and it is why we do not observe it, except under annealing, showing that SiH_3 is easily formed by $SiH + H_2$ recombination. We have searched for $SiHD_2$ and SiH_2D without success. However we have worked in diluted samples where the H_2 (D_2) has to migrate less to recombine with the radical coming from the same parent SiH (SiD) than to find another one; furthermore the 600−700 cm^{-1} region is crowded with the absorption bands of SiD_4, SiD_3HgD, and Si_2D_6 and the weak bands of $SiHD_2$ and SiH_2D may be difficult to find.

The two-photon dissociation of SiH_3HgH may also produce the SiH_2 radical. However we have not been able to find HgH_2 in the Kr matrix. Even if more species are needed in Kr matrixes to identify the HgH_2 molecule than in nitrogen where the lines are much sharper, this means that if this mechanism exists either it is a minor one or the H atoms escape from the cage so that they cannot react afterward with Hg to give the HgH_2 molecule, if not produced in the first reaction. Thus the reaction $SiH_3HgH \rightarrow SiH_2 + HgH_2$ does not happen, and if $SiH_3HgH \rightarrow SiH_2 + Hg + H_2$ (or H + H) takes place, either the hydrogen atoms or molecule leave the cage and SiH_2 stays stable or SiH_2 recombines with hydrogen to give SiH_4 prior to $Hg + H_2 \rightarrow HgH_2$ reaction. To conclude, we think that the formation of SiH_2 directly from SiH_4 by the first process is likely to occur since we observe growing absorption of the radical throughout the irradiation, although we have no proof in favor or against the second possible mechanism.

Why do not we observe the same radicals in the argon matrixes? We think that it is because the KrF laser (248.5 nm) coincides much better with the absorption of Hg in krypton (249.5 nm) than in argon (246 nm),[13] giving a better chance of a two-photon absorption. It is known[6] that the spectra of silane in argon and krypton matrixes show two main sites and we observed that in the SiH stretching frequency (ν_3) region the lowest frequency band has the largest intensity in Ar and the smallest in Kr. As in an argon matrix, the distance is smaller between the atoms than in a Kr matrix; we think that the SiH_4 molecule, which is larger than the Ar atoms, needs two substitutional sites in this matrix. Therefore we assigned the higher frequency to a SiH_4 replacing one atom and the lowest frequency to a SiH_4 molecule replacing two atoms (less repulsive forces from the atoms of the matrix giving lower frequency). We cannot completely exclude that this difference in the geometry of the sites occupied by SiH_4 plays a role in the difference in the yield of insertion product in the two different matrixes. As a matter of fact it may be easier for Hg* to insert when more space is available around the SiH bond, if, as we suppose, the mechanism is the same as in the $Hg^* + H_2$ reaction where the Hg* insertion takes place in the C_{2v} geometry (Hg approaching perpendicular to the H−H bond). When the SiH_4 molecule occupies a double site substitution place, more space around the SiH_4 molecule may favor the increase of the Si−H bond length and thus the insertion of mercury, i.e., the repulsive force of the cage is smaller.

In the nitrogen matrix the IR absorption of silane assigned to the two different sites are not well separated, and the laser is in good coincidence with the Hg absorption, so it would seem a nice system to observe the two-photon absorption leading to radical formation, but it is not the case! This system is effective in only a few samples and with very high laser power where tiny traces of radicals may be imagined in the noise at the same time with HgH_2, which is easier to detect by its sharp lines. However this system is complicated by the E → V transfer from Hg* to N_2[33] that competes with the two-photon absorption mechanism, so that it is difficult to compare the nitrogen case to the rare gas matrixes.

3.5. $SiH_4/CH_4/Hg$. Two experiments have been done to compare the ratio of the insertion of Hg* in SiH_4 and CH_4, the insertion in methane has been studied previously.[5]

(1) A mixed $SiH_4/CH_4/Kr$ 1:1:1000 sample doped with mercury. At this low concentration the Hg atom has no more than one molecule, SiH_4 or CH_4 , in the first shell; irradiated with the KrF laser, the insertion products are formed and the ratio of the CH_3HgH/SiH_3HgH increases with the irradiation time from zero after 500 laser pulses to 0.25 after 7700 pulses. This confirms that the Hg insertion is much easier in silane than in methane. After 1700 pulses the SiH_3HgH absorption reaches a plateau, whereas the CH_3HgH is still growing up after 7700 laser pulses. If the irradiation was not producing any dissociation of the insertion products, the ratio of the intensity of these products should reach unity. This is not so, and to enhance the effect, after 7700 pulses irradiation we gently focalized the laser for 3000 more pulses, giving a decrease of the absorption of 4% for SiH_3HgH and 35% for CH_3HgH. This shows that CH_3HgH is easier to dissociate than SiH_3HgH.

As discussed previously, SiH, SiH_2, and CH_3 radicals have been observed, with growing absorption during the whole experiment.

(2) A mixed SiH_4/CH_4 1:1 sample doped with mercury. In this experiment the mercury atoms have SiH_4 and CH_4 as first neighbors and the ratio of the absorption of the insertion products SiH_3HgH/CH_3HgH is about 100, which means that it is approximately a hundred times easier to insert Hg* in silane than in methane.

4. Conclusion

We have studied the insertion of mercury, excited to the $^3P_1$ state, into the SiH (SiD) bond of the $h_4 - d_4$- silane molecule in nitrogen, argon, and krypton matrixes. We have observed the products of the reactions by their FTIR spectra. Two kind of reactions have been evidenced: a one-photon process producing the new species SiH_3HgH and SiD_3HgD and disilane molecules, and, in Kr matrixes only, a two-photon process producing SiH and SiH_2 radicals. As predicted by Breckenridge[1] and Siegbahn,[3] the insertion reaction takes place without activation energy and therefore the H and D compounds are formed with the same yield. The SiH_3HgH or SiD_3HgD molecules close to the parent molecules produced Si_2H_6 or Si_2D_6 under KrF laser irradiation, and this process takes place probably through a small barrier—the deuterated compound dissociating less than the hydrogenated one.

In the Kr matrix under high power KrF laser irradiation, we observe less production of the insertion compounds than in Ar matrixes but an important production of SiH (SiD) and SiH_2 (SiD_2) radicals by a two-photon process. Upon annealing, these radicals recombine with the hydrogen which migrates in the matrix, and the SiH_3 (SiD_3) radical is formed. This SiH_3 (SiD_3)

radical is further dissociated under KrF irradiation showing that it is absorbing light in the 5 eV range.

These experiments have shown very different results in Ar and Kr matrixes. In Kr matrix, where a majority of the silane molecules replaces one Kr atom, the production of the insertion product is less than in Ar where the silane molecule mainly replaces two argon atoms. This difference may indicate that the relative positions of Hg* and SiH_4 play an important role in the insertion reaction, making it easier when more space is allowed around the SiH bond.

These experiments have led to a better understanding of the pioneer experiments on the radicals in argon matrixes.[8−10] They have shown that the IR absorption of SiH_3 does not lie in the same range as the ν_1 and ν_3 vibrations of SiH_2. The processes of formation of the different products have been discussed.

Finally, the relative rates of formation of the insertion products with CH_4 or SiH_4 have been evaluated by measurements in mixed SiH_4/CH_4 matrixes doped with Hg and diluted or not in krypton. These last experiments have shown that the insertion of Hg* is about 100 times easier in SiH_4 than in CH_4.

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