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Free radicals formed by reaction of silane with hydrogen atoms in rare gas matrices at very low temperatures

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The radicals formed by the reaction of SiH_4 with H produced by the photolysis of HI in the matrices of Xe and Kr were investigated by electron spin resonance (ESR) spectroscopy at the temperatures between 4.2 and 100 K. The radicals observed were identified as SiH_3 and SiH_5. The newly observed radical SiH_5 is considered as the intermediate of the reaction $SiH_4 + H \rightarrow SiH_3 + H_2$. The radical had two conformers; both were observed in a Xe matrix, while only one was observed in a Kr matrix. The ESR parameters of these radicals were determined by numerical deconvolution of the observed spectra. The hyperfine coupling of ^{29}Si in silyl radicals isolated in Kr was determined accurately by the present method of the radical formation. The value obtained was 189.5 G instead of 266 G previously reported.

I. INTRODUCTION

Physical and chemical properties of silicon compounds have been extensively studied because of the wide variety of their practical applications. The characteristic nature of these compounds is closely related to the fact that silicon atoms are able to have higher coordination number than four.[1] Simple five-coordinated silicon compounds are known to be unstable except for such fluorinated ones as $R\text{-}SiF_4^-$ (R is an alkyl radical), but are important as intermediates in the reactions to form more stable six-coordination compounds.[2] The fundamental five-coordinated radical SiH_5 has not yet been observed, but was discussed by Glasgow *et al.*[3] as the intermediate of the following reaction:

$$SiH_4 + H \rightarrow SiH_3 + H_2. \quad (1)$$

A spectroscopic observation of SiH_5, if possible, would, therefore, be of great interest for the elucidation of its role in the chemical process as well as for the understanding of its electronic state.

Reactions of atomic hydrogen with organic compounds in low temperature matrices have been studied extensively by electron spin resonance (ESR) spectroscopy.[4] Previously, we have studied the reaction of PH_3 with H produced by the photolysis of HI in the Xe matrix at 4.2 K and found that PH_4 is formed as intermediate in the reaction $PH_3 + H \rightarrow PH_2 + H_2$.[5] In the present work, we report the ESR spectra of SiH_5 and SiH_3 formed by the reaction of SiH_4 with H in Xe and Kr matrices.

II. EXPERIMENTAL

The matrix substances (Xe and Kr) and H_2 obtained from Takachiho Co. and I_2 from Koso Chemical Co. were used without further purification. The SiH_4 was kindly supplied by Professor Matsumura of this Institute. The hydrogen iodide was synthesized from H_2 and I_2 by catalytic reaction on platinized asbestos. Gaseous mixtures of Xe, SiH_4, and HI were condensed in an ESR quartz tube at 77 K. For the Kr matrix, because of the low melting point, the gaseous mixtures were directly introduced into the ESR tube immersed in the liquid helium. For measurements with the Kr matrix, a special cryostat was used, whose bottom was connected to a quartz tube which could be inserted into the cavity of ESR spectrometer. The concentrations of SiH_4 and HI were varied from 0.001 to 0.1 mol %.

Photolysis was carried out with a high pressure mercury lamp with a filter (I_2–KI solution) to cut off the light with wavelengths shorter than 250 nm. The spectrometer used for ESR measurement was a JES-RE2XG equipped with an Oxford Instruments ESR-900 temperature control system. The resonance frequency and magnetic field were monitored by a TR-5211C frequency counter and a PMR field meter.

III. RESULTS

When the rare gas matrices containing only SiH_4 were irradiated by the light of wavelengths longer than 250 nm, no ESR spectra appeared. Upon the addition of HI to the matrices, characteristic spectra appeared, which were strongly dependent on both the matrix used and the temperature.

A. Xe matrix

Figure 1 shows a typical example of an ESR spectrum of a Xe/SiH_4 (0.3 mol %)/HI(0.1 mol %) mixture photolyzed at 4.2 K for 5 min. The intense outer doublet with about 500 G splitting is characteristic of trapped H atoms, which exhibit superhyperfine structures arising from the coupling with the magnetic nuclei of ^{129}Xe and ^{131}Xe.[6] The central part of the spectrum, expanded at slow sweep, is displayed in Fig. 2(a). The spectrum consists of three components: (I) a quartet of triplets, (II) a doublet of quintets, and (III) a broad singlet. Figure 2(b) shows the computer simulation, using the ESR parameters given in Table I with the mixing ratio of I:II:III = 1:3:4 and the Gaussian linewidths of three components: 1.9, 5.5, and 10.0 G, respectively.

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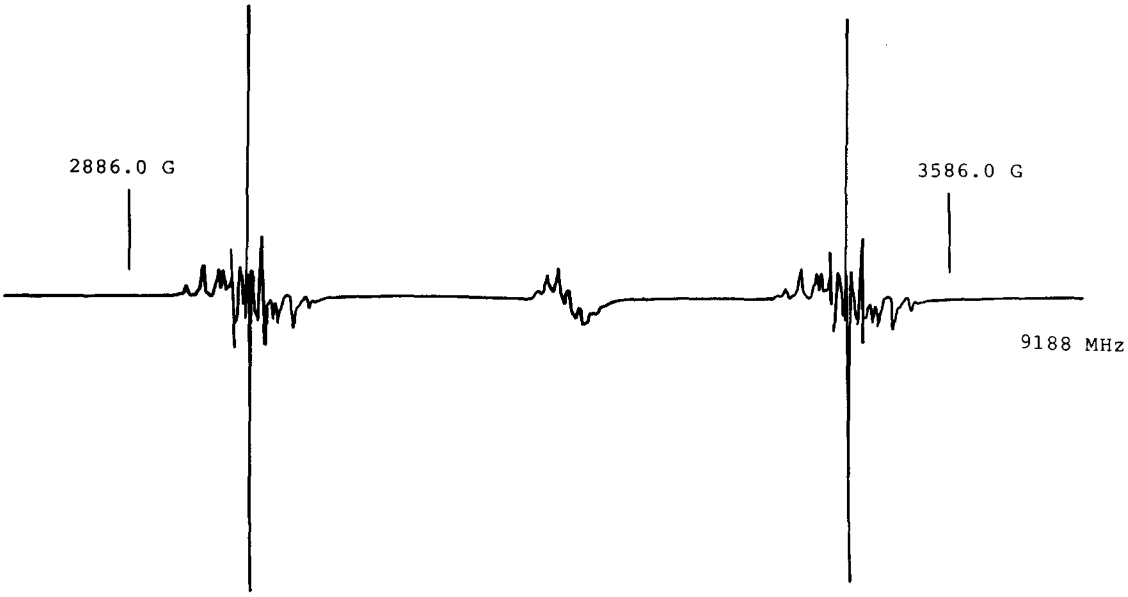

FIG. 1. The ESR spectrum obtained from the Xe/SiH_4 (0.3 mol %)/HI(0.1 mol %) mixture after photolysis at 4.2 K.

On warming the sample, these three components varied irreversibly, as shown in Figs. 3(a)–3(d). Little change could be observed up to 35 K [Fig. 3(a)]. When the sample was kept at 40 K, the signal of trapped H atoms and the spectrum II disappeared with the concomitant increase of the spectrum III. The spectrum I also decreased, but a trace of it remained even after long annealing [Fig. 3(b)]. Figure 3(c) shows the spectrum obtained by annealing at 77 K. The wide range scan of this spectrum is shown in Fig. 3(d) which clearly exhibits extra lines with a large splitting probably due to the coupling with ^{29}Si.

B. Kr matrix

Figure 4 shows the spectrum from a Kr/SiH_4 (0.3 mol %)/HI(0.1 mol %) mixture photolyzed at 4.2 K for 5

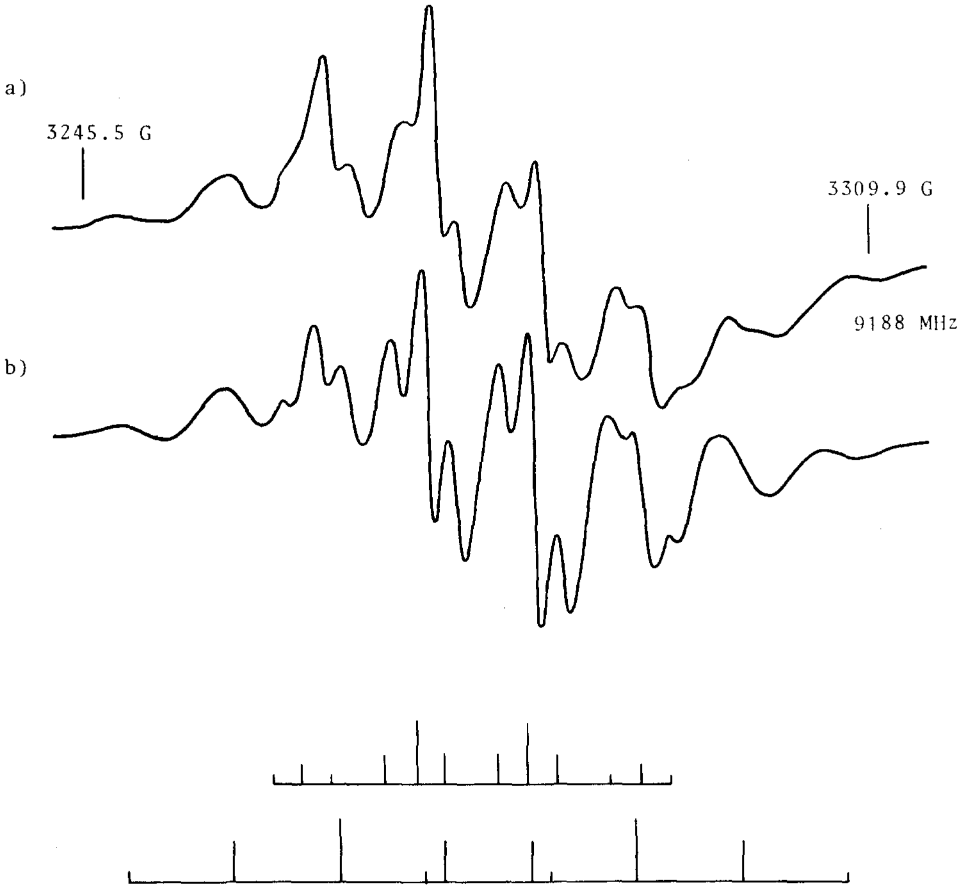

FIG. 2. The expanded ESR spectra of the central part of the spectrum shown in Fig. 1: (a) the observed spectrum; (b) the simulated spectrum. The stick diagram indicates the hyperfine line positions for the spectra I and II.

TABLE I. ESR parameters for SiH_5 and SiH_3 radicals.

Matrix	Spectrum	*g* factors	Hyperfine couplings (G)		Radical	Reference
Xe	I	2.002 4	9.30 (3H)	2.45 (2H)	SiH_5 (D_{3h})	This work
	II	2.001 6	8.70 (4H)	24.50 (1H)	SiH_5 (C_{4v})	This work
	III	2.003 0	8.10(3H)	184.3 (^{29}Si)	SiH_3	This work
		2.003 0		190 (^{29}Si)	SiH_3	10
Kr	V	2.001 4	7.98 (3H)	2.45 (2H)	SiH_5 (D_{3h})	This work
		$g_{\parallel} = 2.001\,2$	$A_{\parallel} = 8.15$ (3H)	189.5 (^{29}Si)		
	IV	$g_{\perp} = 1.001\,3$	$A_{\perp} = 7.84$ (3H)		SiH_3	This work
		$g_{iso} = 2.001\,27$	$A_{iso} = 7.94$ (3H)			
		$g_{\parallel} = 2.001\,2$	$A_{\parallel} = 8.1$ (3H)			
		$g_{\perp} = 2.001\,4$	$A_{\perp} = 7.4$ (3H)		SiH_3	11
		$g_{iso} = 2.001\,3$	$A_{iso} = 7.63$ (3H)			
		$g_{\parallel} = 2.003$	8.10 (3H)	266 (^{29}Si)	SiH_3	9
		$g_{\perp} = 2.007$				

min. The spectrum is similar to that observed with the Xe matrix. The central part obtained immediately after photolysis is expanded in Fig. 5(a). In order to change the temperature of the irradiated sample of Kr matrix, the sample tube was taken out of the liquid helium surface for a while and replaced back into the original position for the next ESR measurement. The spectra shown in Figs. 5(b) and 5(c) were obtained by this annealing procedure. The difference

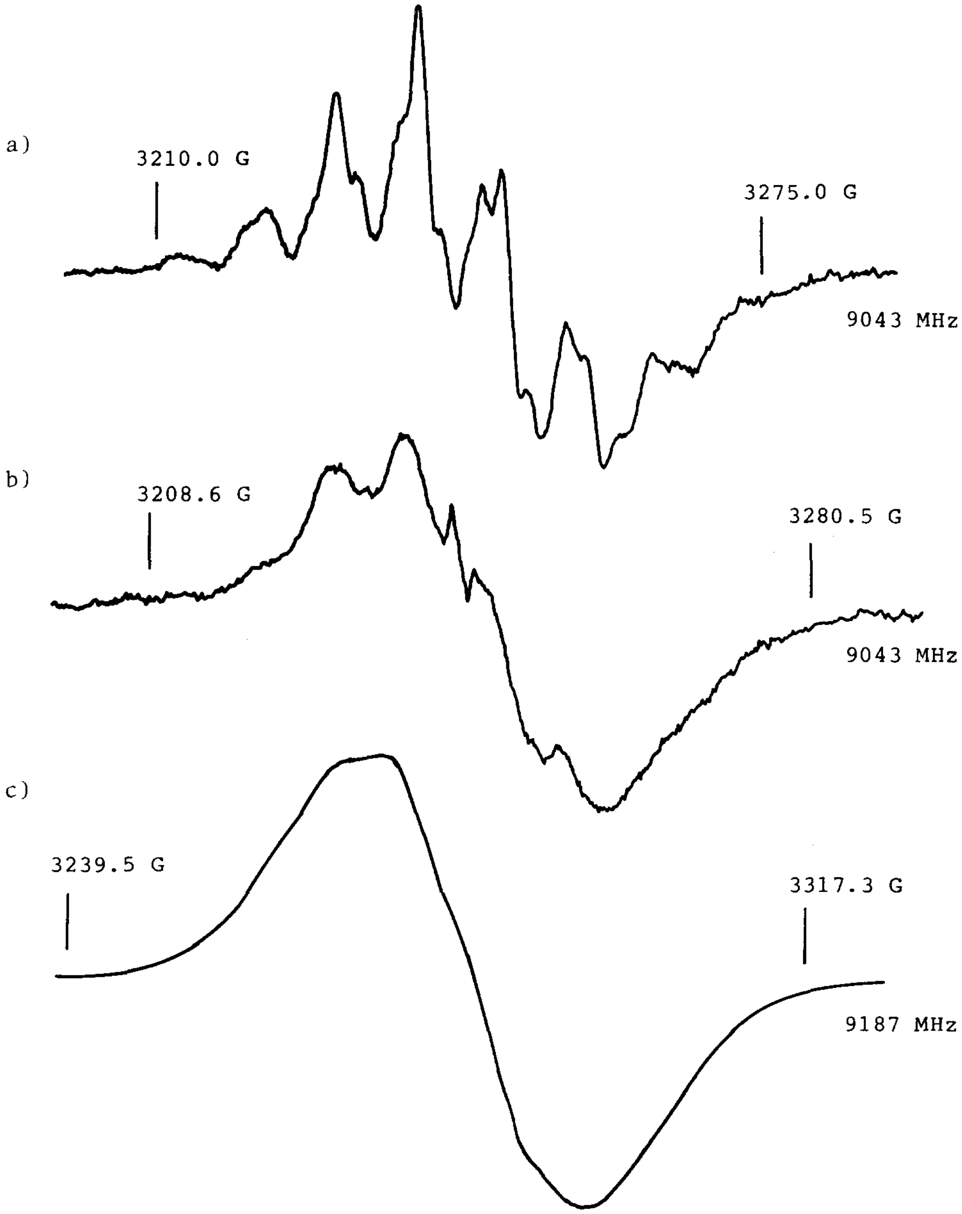

FIG. 3. The change of the ESR spectrum shown in Fig. 2 by thermal annealing: (a) after annealing at 35 K; (b) at 40 K; (c) at 77 K; (d) the wide range scan of (c).

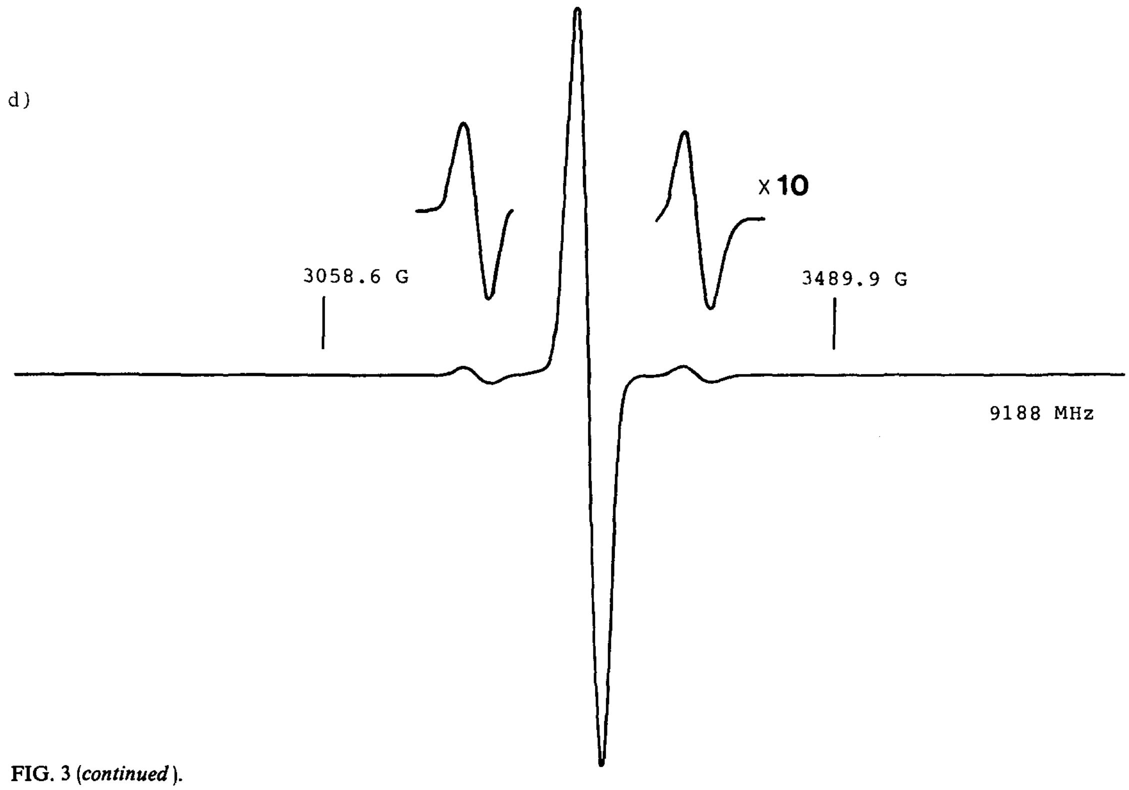

FIG. 3 (*continued*).

between the two spectra resulted from different time intervals during which the sample was kept above the liquid helium surface. It may be noticed that the center portion of Fig. 5(b) resembles the quartet of triplets observed in Fig. 2, and that the resolution of the spectrum is enhanced by annealing.

The spectrum shown in Fig. 5(c) consists of two components: (IV) a sharp quartet and (V) a broad quartet of triplets. Figure 5(d) shows the computer simulation, using the parameters listed in Table I with the mixing ratio of 1:7 and the Gaussian linewidths of 0.7 and 2.0 G, respectively. By

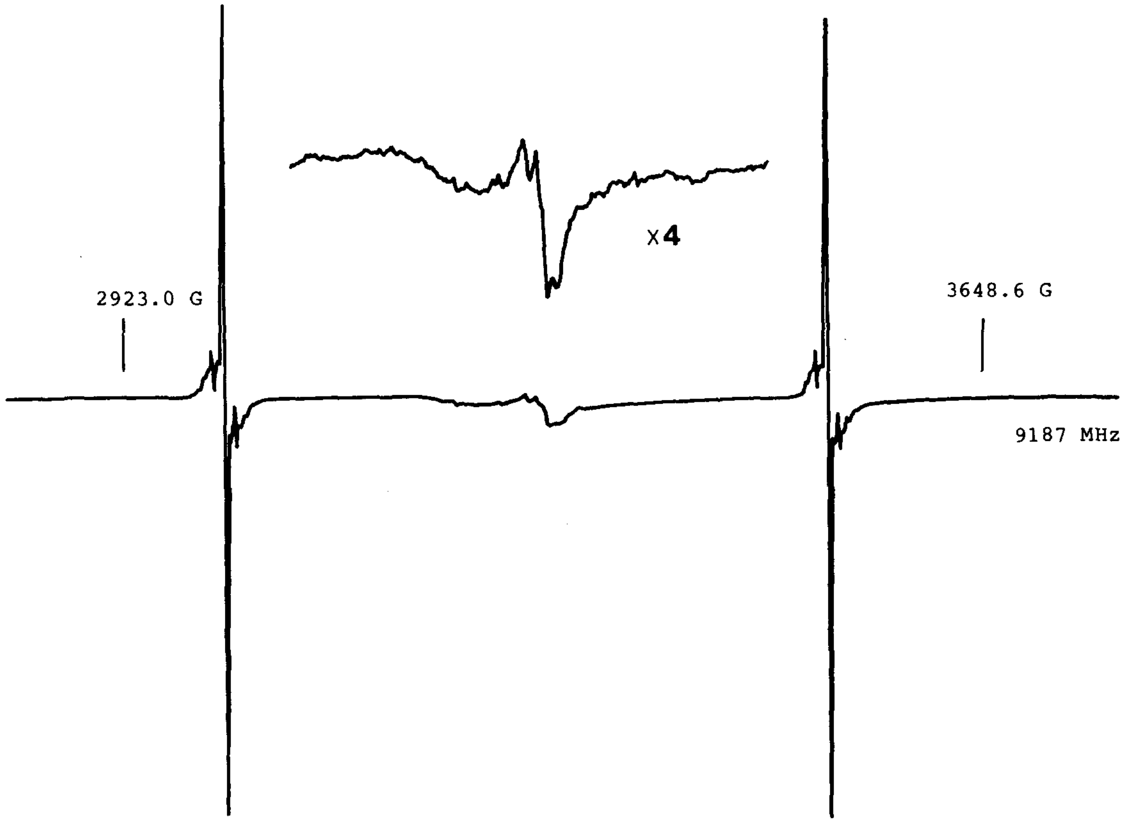

FIG. 4. The ESR spectrum obtained from the Kr/SiH_4 (0.3 mol %)/HI(0.1 mol %) mixture after photolysis at 4.2 K.

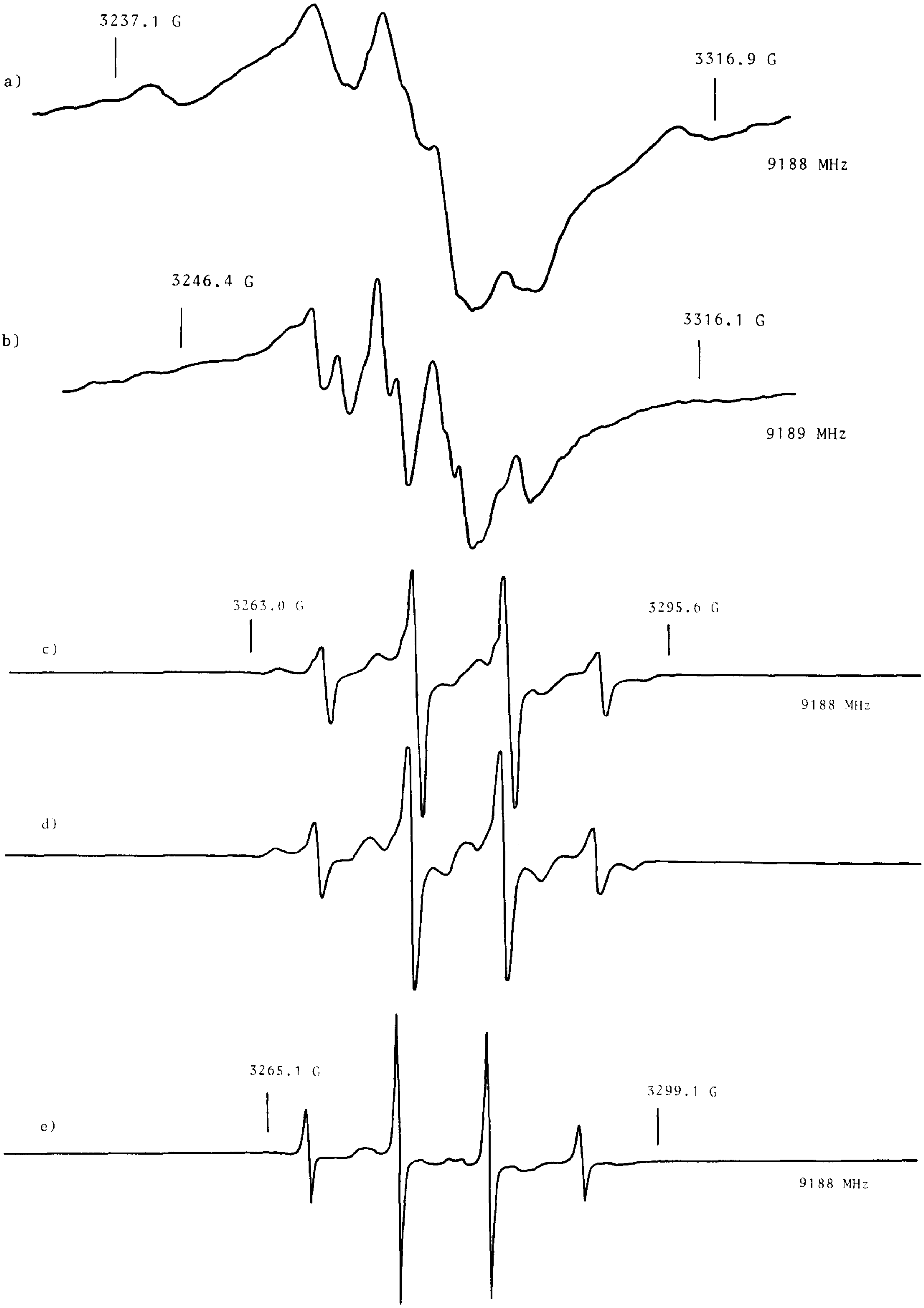

FIG. 5. The change of the central part of the spectrum shown in Fig. 4 by thermal annealing: (a) immediately after photolysis; (b) after keeping the sample tube above the liquid helium surface for 30 s; (c) for 5 min; (e) for 15 min; (d) the simulated spectrum for (c).

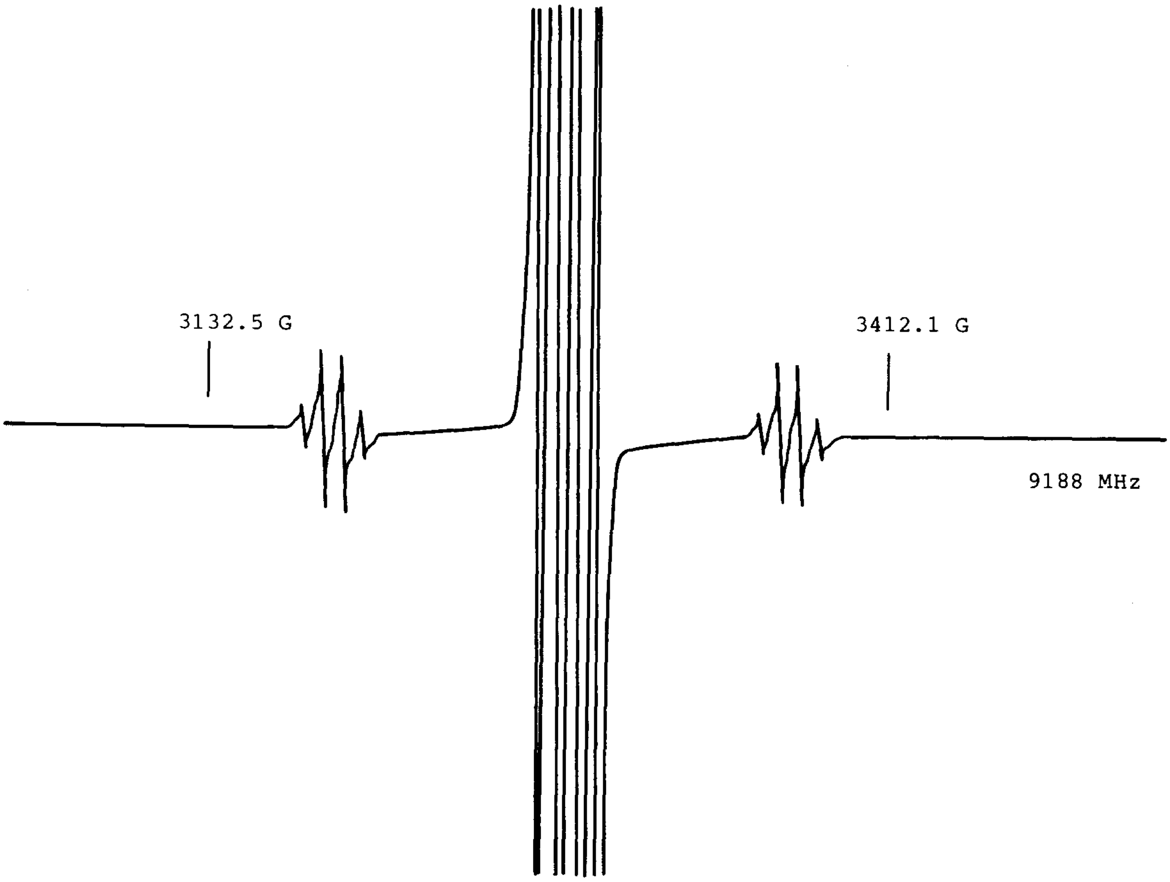

FIG. 6. The wide scan spectrum of Fig. 5(e).

further annealing, the spectrum V disappeared but the well resolved spectrum IV remained, as shown in Fig. 5(e). Figure 6 shows the wide range scan of Fig. 5(e). In addition to the main central quartet, small but distinct quartet spectra with the spacing of 7.94 G appear on both sides of the main quartet with the splitting of 189.5 G, which must be due to the coupling with ^{29}Si in the SiH_3 radical. The ESR parameters determined are listed in Table I along with those previously reported.[7–12]

IV. DISCUSSION

As has been reported by Gordy *et al.*,[9,10] and Raghunathan and Shimokoshi,[11] the spectrum of SiH_3 is dependent on the matrix used. Generally, in the Xe matrix, resolution is poor, possibly because of the strong interaction of unpaired electrons with the magnetic nuclei of Xe. The spectrum III shown in Fig. 3(c) is much the same as those reported for SiH_3, though the present spectrum has shoulders, suggesting a little better resolution than those previously reported. The spectrum obtained by the photolysis of the SiH_4/HI mixture in the Kr matrix [Fig. 5(e)] is a well resolved quartet with the splitting reported for SiH_3. Therefore, the spectrum III obtained by the photolysis of the same mixture in the Xe matrix may be identified as SiH_3.

In addition to SiH_3, the spectra I and II were observed immediately after photolysis, and thermal annealing decreased their intensities and concomitantly increased the intensity of the spectrum III, suggesting that the products primarily formed were converted to SiH_3. These results indicate that the reaction of $H + SiH_4$ at low temperatures produces some intermediate complexes. The most plausible candidate for this intermediate is SiH_5. Glasgow *et al.* studied the reaction between D atoms and SiH_4, and concluded that abstraction reaction is less probable than the addition reaction as the gas-phase primary process. If this is the case, it is very likely that the addition product SiH_5 is stabilized in low temperature matrices.

The dimeric species Si_2H_5 might be formed by the following reaction by silyl radicals:

$$SiH_3 + SiH_4 \rightarrow SiH_2SiH_3 + H_2 \tag{2}$$

or

$$SiH_3 + SiH_3 \rightarrow SiH_2SiH_3 + H \tag{3}$$

is another candidate responsible for the spectra I and II. However, the relative intensities of I and II to that of III were not enhanced by increasing the initial concentration of SiH_4 in the matrices. The spectra I and II, therefore, cannot be due to the dimeric species.

The spectra assigned as the quartet of triplets (I) and the doublet of quartets (II) are reasonably considered to be originated from two sets of five protons: (I) $H_a \times 2 + H_b \times 3$ and (II) $H_a \times 1 + H_b \times 4$, respectively. This means the presence of two kinds of SiH_5 as the intermediate. The trigonal structure has been reported for most of the five-coordinated silicon compounds.[1] According to the theoretical calculation of Glasgow *et al.*,[3] SiH_5 is able to take another form of

C_{4v}. Thus, we may assign the spectra I and II to the SiH_5 radicals with the structure of D_{3h} and C_{4v}, respectively.

In the Kr matrix, we could not observe the doublet of quintets corresponding to the C_{4v} structure, but only the quartet of triplets corresponding to the D_{3h} structure of SiH_5 along with the well resolved quartet spectrum of SiH_3. In the Xe matrix, thermal annealing effected the elimination of the spectrum II more rapidly than that of the spectrum I, which suggests that C_{4v} structure is less stable than D_{3h} in the rare gas matrices.

The molecular orbital calculations with the CNDO approximation[5,13] were performed on various structures of SiH_5. The optimized geometries obtained were D_{3h}, C_{4v}, and C_{3v}, among which the radical with C_{3v} symmetry had the least stabilizing energy. These results were in good agreement with those reported by Glasgow *et al.*, and consistent with the present observation.

As has been reported,[5,14] the ESR line shapes of small hydride radicals are dependent on the matrix and the temperature because of their rotational states. For example, SiH_3 isolated in the Ar matrix gives a quartet spectrum of the 1:1:1:1 intensity ratio with anomalous linewidths, instead of the binomial of 1:3:3:1 usually observed. The low resolution of the spectrum of SiH_3 observed in the Xe matrix, therefore, is probably not only due to the large nuclear moment of Xe, but also due to the rotational effect. On the other hand, in the case of SiH_5 in Xe, we could observe the well resolved spectra. Possible reasons are (a) the hyperfine couplings of protons are larger than those of SiH_3, and (b) the interactions of atomic hydrogen with SiH_4 in the stabilized form might restrict the motion of the complex in Xe.

The present method to produce SiH_3 radicals by the reaction between H and SiH_4 was so efficient that we could obtain the ^{29}Si coupling accurately from the observed $^{29}SiH_3$ spectrum. As is well known,[6–8,10,12] the form of the SiH_3 radical is pyramidal and the ^{29}Si coupling gives the information on the deformation from the plane structure. The ^{29}Si coupling reported for SiH_3 and methyl-substituted silyl radicals in the liquid and solid phases are all in the range of 180–190 G, except for the $^{29}SiH_3$ isolated in the Kr matrix (266 G).[9] However, in the present experiments we obtained the coupling constant of 189.5 G for $^{29}SiH_3$ in Kr, as listed in Table I. Therefore, the ordinary values of 180–190 G for ^{29}Si coupling were confirmed even in the radical isolated in Kr.

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