Transition Moment of the $A^2\Delta$ - $X^2\Pi$ System of SiH Studied by Laser Induced Fluorescence Spectroscopy in Supersonic Free Expansions

Masaru FUKUSHIMA[†], Takashi ISHIWATA*, and Kinichi OBI^{*,††}

Advanced Technology Research Center, Mitsubishi Heavy Industries, LTD.

Sachiura, Kanazawa-ku, Yokohama, Kanagawa 236-0003

*Department of Information Sciences, Hiroshima City University, Asa-Minami-ku, Hiroshima 731-3194

**Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152-8551

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Laser induced fluorescence (LIF) excitation spectra of the $A^2\Delta$ - $X^2\Pi$ transition of SiH have been measured in supersonic free expansions. We observed the eight vibronic bands, 0-0, 1-0, 0-1, 1-1, 2-1, 1-2, 2-2, and 2-3, the three $\Delta v = -1$ bands of which were observed for the first time. The $\Delta v = 0$ sequence dominates the spectra, because of favorable Franck-Condon (F-C) factors. On the other hand, the intensities of the $\Delta v = -1$ transitions are much weaker than those of the $\Delta v = +1$ transitions in spite of the considerable intensity of $\Delta v = -1$ expected from the calculated F-C factors. This behavior is interpreted in terms of the transition moment having the strong dependence on internuclear distance.

Key Words: Laser induced fluorescence spectroscopy, SiH radical, Franck-Condon factor, Electronic transition moment, Fluorescence lifetime

1. Introduction

The SiH radical is one of the most important chemical species on the manufacturing processes of silicon devices, such as chemical vapor deposition (CVD) and chemical beam epitaxy (CBE) processes.¹⁻³⁾ To explore the chemical reaction mechanism in these processes, quantitative measurement of the SiH radical under the pilot condition is thought to be quite helpful. In practical manufacturing processes, SiH concentration monitoring under operating conditions is also a key technique to optimize and control these processes and for product quality assurance.

Spectroscopic measurement is the best way to explore the processes under operating conditions, since it is only the way of *in situ* diagnostic method, *i.e.* the observation method without any disturbance to the object condition. To estimate the concentration of chemical species by spectroscopic techniques, such as absorption and fluorescence, it is indispensable to know the dipole moment associated with the transition. In describing the transition moment, M_{ev} , of the vibronic transition from the ground state, $\psi_{e'v'} = \psi_e'(r, R) \psi_v'(R)$, to the excited state, $\psi_{e''v''} = \psi_e''(r, R) \psi_v''(R)$, of diatomic molecules, we usually adopt the Franck-Condon (F-C) approximation. Under the approximation it is assumed that the transition moment is independent of the locations of the nuclei, and the intensity distribution of the vibronic bands is evaluated by the square of the overlap integral between upper and lower vibrational wave functions, the F-C factor:

$$\begin{aligned} M_{ev} &= \int \psi_{e'v'}^* \mu \psi_{e''v''} d\tau \\ &= \langle \psi_v'(R) | \langle \psi_e'(r, R) | \mu(r, R) | \psi_e''(r, R) \rangle | \psi_v''(R) \rangle \\ &= \langle v' | R_e(R) | v'' \rangle \\ &= R_e \langle v' | v'' \rangle \end{aligned} \quad (1)$$

where $R_e(R)$ is $\langle \psi_e' | \mu(r, R) | \psi_e'' \rangle$ and v' and v'' are abbreviations for ψ_v' and ψ_v'' , respectively. A number of spectroscopic studies for the $A^2\Delta$ and $X^2\Pi$ states of the SiH radical have been reported^{4,6-15)}, it was reported that the equilibrium internuclear distance of the adiabatic potentials are close to each other. The calculated F-C factor indicates:

1. the $\Delta v = 0$ transitions have the most dominant F-C factor,
2. the $\Delta v = \pm 1$ transitions have comparable F-C factor,
3. the other transitions, $\Delta v \geq 2$, are almost negligible.

However, the $\Delta v = -1$ transitions have never been observed, while the $\Delta v = +1$ transitions have been reported. In this work, we have resolved the vibronic bands of the $A^2\Delta$ - $X^2\Pi$ transition of SiH, owing to the great advantages of the supersonic free expansion condition, and we have observed the $\Delta v = -1$ transitions for the first time. We found the intensity of the $\Delta v = -1$ transitions weaker than that expected from the calculated F-C factors, *i.e.* a discrepancy between the observed and predicted vibronic band intensity distribution. The discrepancy was interpreted as insufficient description of the transition moment by the F-C approximation. Using the vibrational wave functions

[†] Present address: Department of Information Sciences, Hiroshima City University, Asa-Minami-ku, Hiroshima 731-3194

^{††} Present address: Department of Chemical and Biological Sciences, Japan Woman's University, Mejirodai, Bunkyo-ku, Tokyo 112-8681

derived from the Morse potentials and the transition moment obtained from the *ab initio* calculation,²⁵⁾ we demonstrate the reproduction of the intensity distribution of the observed vibronic band by the higher approximation level, the *r*-centroid approximation and the numerical integration of Eqn. (1).

2. Experiment

The experimental setup used in this study is described in detail elsewhere¹⁶⁻²⁰⁾. The SiH radical was generated by ArF laser photolysis of phenylsilane, C₆H₅SiH₃. The Ar gas containing phenylsilane at the saturated vapor pressure at room temperature was expanded into a vacuum chamber through a pulsed valve with a 800 μm orifice operated at 10 Hz. The pulsed jet was irradiated with the ArF laser just after the orifice to generate the radical. The ArF laser was tightly focused on the jet. The LIF was observed ~ 40 mm downstream from the photolysis point by a photo-multiplier (Hamamatsu, R928). The photo-current signals were treated by a gated integrator (PAR, 9821B) after current amplification. The signals were normalized with the intensity of probe laser at each shot. The excitation laser for the LIF measurement was a N₂ laser pumped dye laser (Moletron, UV-22 and DL-14) with an energy resolution of ~ 0.2 cm⁻¹. The laser wavelength was calibrated using opt-galvanic lines of He and Ne recorded simultaneously. The time profiles of the LIF signals were recorded using a wave memory (Iwatsu, DM-901) and processed using a personal computer. Phenylsilane (Shin-Etsu Chemical, GR Grade) and the Ar carrier gas (Nippon Sanso, Research Purity) were used without further purification.

3. Results

We have observed eight vibronic bands, 0-0, 1-0, 0-1, 1-1, 2-1, 1-2, 2-2, and 2-3, of the A²Δ - X²Π transition of SiH. Among them, the three Δ*v* = - 1 bands were detected for the first time in this study. The vibronic bands terminating on *v*' > 2 could not be observed, because of the predissociation in the A²Δ state.^{15,21)} Figure 1 shows the LIF excitation spectra of the 0-1, 1-1, and 2-1 bands sharing the same initial state, *v*" = 1. The vibrational and rotational assignments were carried out using the known molecular constants of the X²Π and A²Δ states of SiH.²²⁾ From the rotational analysis, the rotational temperature is estimated to be about 25 K.

The time profiles of the LIF from the *v*' = 0, 1, and 2 levels of the A²Δ state were measured at the lowest rotational levels, *J* = 5/2 and 3/2 for the *F*₁ and *F*₂ states, respectively, to derive the fluorescence lifetime, τ_f. The time profiles of fluorescence were analyzed by assuming exponential decay;

$$I_f(t) = I_f^0 \cdot \exp\left(-\frac{1}{\tau_f} \cdot t\right), \quad (2)$$

where *I_f*(*t*) is the fluorescence intensity at time, *t*, after the laser excitation pulse, and *I_f*⁰ is the intensity at *t* = 0. Our analysis showed no systematic deviation in the residual indicating no complicated functional dependence in the fluorescence decay. The measured fluorescence lifetimes of the A²Δ state of SiH are summarized in Table 1.

4. Discussion

To discuss the observed vibronic band intensity distribution, we calculate the F-C factors of the A²Δ - X²Π transition of SiH based on the Morse potential²³⁾;

$$\begin{aligned} U(x) &= D_e \{1 - \exp(-\beta x)\}^2, \\ x &= r - r_e, \\ D_e &= \frac{\omega_e^2}{4\omega_e x_e}, \\ \beta &= \omega_e \left(\frac{2\pi^2 c \mu}{D_e h N_A} \right)^{1/2} = 1.21777 \times 10^7 \omega_e \sqrt{\frac{\mu}{D_e}} \end{aligned} \quad (3)$$

where *r* is internuclear distance*¹, *r_e* is nuclear equilibrium position, ω_e and ω_e*x_e* are vibrational molecular constants, μ is reduced mass, *h* is Planck constant, *c* is the speed of light, *N_A* is Avogadro's number.

The constant, 1.21777 × 10⁷, is in units of cm⁻¹, Å, and atomic mass units. The Morse potentials of the A²Δ and X²Π states of SiH are shown in Fig.2, and the molecular constants used for calculation of the Morse potentials are listed in Table 2.²²⁾ To obtain the vibrational wave functions for the Morse potentials, we used the following formulas²⁴⁾:

$$\psi_{v=0} = N_0 \exp\left\{ \frac{(x_e - 1)\delta - \exp(-\delta)}{2x_e} \right\} \quad (4)$$

$$\psi_{v=n} = (-1)^n N_n \psi_0 \left[1 + \sum_{i=1}^n C_i \left\{ \prod_{j=1}^i \langle (n+j)x_e - 1 \rangle \right\} R^i \right] \quad (5)$$

where δ = (*r* - *r_e*)β, *R* = exp(δ), *x_e* = ω_e*x_e*/ω_e, and *N₀* and *N_n* are normalization constants. The F-C factors were calculated using a numerical integration procedure of the obtained wave functions. The calculated F-C factors are listed in Table 3.

Among the Δ*v* = - 1, 0, and 1 vibronic transitions originating from the *v*" = 1 vibrational state shown in Fig.1, the 1-1 band is the strongest, and the 2-1 band is two or three times weaker than the 1-1 band, while the 0-1 band is by about two orders of magnitude weaker, *i.e.* *I*₁₋₁ > *I*₂₋₁ >> *I*₀₋₁. For the other vibronic

Table 1 Observed fluorescence lifetimes of the SiH, A²Δ state.^a

<i>v</i> '	<i>F</i> ₁ state	<i>F</i> ₂ state
0	559	530
1	684	621
2	—	368

^a in ns.

Table 2 Molecular constants used in the present calculation.

ω _e '	1858.90	cm ⁻¹
ω _e <i>x_e</i> '	99.175	cm ⁻¹
<i>r_e</i> '	1.52347	Å
ω _e "	2041.80	cm ⁻¹
ω _e <i>x_e</i> "	35.51	cm ⁻¹
<i>r_e</i> "	1.52010	Å

*¹ According to custom, the internuclear distance is expressed by *r* hereafter. In the previous sections, it was denoted by *R* and the position of electrons in the molecule was shown by *r*.

Table 3 Calculated Franck-Condon factors (upper) and r -centroids (lower) of the $A^2\Delta - X^2\Pi$ transition of SiH.

v''/v'	0	1	2	3	4	5
0	0.9879 1.5476	0.1182(-1) 0.7448	0.1056(-3) 4.7648	0.5901(-4) 2.6869	0.2263(-6) 5.9177	0.4705(-5) 0.1248
1	0.1018(-1) 2.5429	0.9064 1.6007	0.8129(-1) 1.2212	0.1880(-2) - 0.0019	0.1023(-4) 11.8262	0.2610(-4) 4.4096
2	0.1646(-2) 1.7868	0.6835(-1) 2.1661	0.6688 1.6513	0.2245 1.4395	0.3256(-1) 1.0992	0.3382(-2) 0.4817
3	0.1889(-3) 2.0957	0.1145(-1) 1.9944	0.1876 2.0680	0.2912 1.6827	0.3176 1.5792	0.1271 1.4279
4	0.3255(-5) 0.4222	0.1856(-2) 2.1171	0.4925(-1) 2.0887	0.2819 2.0511	0.1737 (-1) 1.4681	0.1754 1.6659
5	0.6400 (-5) 1.4088	0.1582(-4) 3.8174	0.1172(-1) 2.1644	0.1366 2.1437	0.1947 2.0686	0.5942(-1) 2.0905

Fig.1 The LIF excitation spectrum of the 0-1, 1-1, and 2-1 vibronic bands of the SiH, $A^2\Delta - X^2\Pi$ transition observed in the supersonic free expansions of Ar.

bands, the observed intensities with the same initial vibronic state show $I_{0-0} > I_{1-0}$ and $I_{2-2} \gg I_{1-2}$. The observed intensity distribution is summarized as $I_{\Delta v=0} > I_{\Delta v=+1} \gg I_{\Delta v=-1}$. On the other hand, the calculated F-C factors indicate $I_{\Delta v=0} > I_{\Delta v=+1} > I_{\Delta v=-1}$ in the low vibronic level region where we are concerning in the present discussion; e.g. $I_{1-1} > I_{2-1} > I_{0-1}$. For this inconsistency between

the observed LIF intensity distribution and the calculated F-C factors, we can generally consider the following two reasons:

1. vibronic level dependent non-radiative processes, such as predissociation and auto-ionization, in the upper state,
2. the strong dependence of the electronic transition moment on the internuclear distance, r .

The first is categorically denied as the reason, because the inconsistency does not depend upon the upper vibronic level, v' , but upon the vibronic transition, Δv . We thus interpret the inconsistency as the insufficiency of the F-C approximation and try to reproduce the intensity distribution by the r -centroid approximation and numerical integration of Eqn. (1), using the reported transition moment, $R_e(r)$.²⁵⁾ In the r -centroid approximation, the transition moment is approximated as follows:

$$M_{ev} = R_e(\bar{r}) \langle v' | v'' \rangle, \quad \bar{r} = \frac{\langle v' | r | v'' \rangle}{\langle v' | v'' \rangle}, \quad (6)$$

where $\bar{r}$ is the weighted center of the internuclear distance for the vibrational wave functions, $R_e(\bar{r})$ is the transition moment at $\bar{r}$, and r is the internuclear distance. The r -centroids, $\bar{r}$, for each vibronic band were evaluated using a numerical integration of the vibrational wave functions. The integration of electronic transition moment using Eqn. (1) was numerically integrated using the vibrational wave functions and the transition moment.

$$M_{ev} = \langle v' | R_e(r) | v'' \rangle \quad (7)$$

For the two higher level calculations, we used the transition moment computed by an *ab initio* method.²⁵⁾ Since the reported values are restricted to certain internuclear distances, r 's, the moment between the distances was interpolated using the third order spline function. The transition moment of the $A^2\Delta - X^2\Pi$ system of SiH used for the calculations are shown in Fig.2 on the Morse potentials, where the reported transition moment is indicated by dots and interpolated ones are represented by a curved line.*² The transition intensities calculated under the r -centroid approximation and the numerical integration of Eqn. (1) are listed in Table 4. It is realized that the transition intensities evaluated by the two methods reproduce the observed

*² A hump appears on the transition moment at about 2.4 Å. This may be due to limitation of the computation, because the $A^2\Delta$ state has a crossing with a repulsive $^4\Pi$ state in this range (private communication with the author of the calculated transition moment, Prof. Mats Larsson, at the 24:th International Symposium on Free Radicals, Tällberg, Sweden, 1997). Since the values of the transition moment in this range are not so large and since the amplitude of wave functions are also small, then the hump would not be so effective for the current calculation.

Fig.2 The Morse potential of SiH computed using the molecular constants listed in Table 2 and the predicted transition moment cited from Ref. 22 (dots). Although at a nuclear distance greater than 3.2 Å, the transition moment curve extrapolated using the cubic spline procedure become negative, we set the negative values to zero.

vibronic band intensity distribution. The success of the reproduction of the observed band intensity distribution by the calculations is direct experimental evidence of the strong nuclear dependence of the transition moment of the SiH, $A^2\Delta - X^2\Pi$ system. The upper $A^2\Delta$ and lower $X^2\Pi$ states of SiH are correlated to $\text{Si}(^1\text{D}) + \text{H}$ and $\text{Si}(^3\text{P}) + \text{H}$, respectively, and the atomic transition between $\text{Si}(^1\text{D})$ and $\text{Si}(^3\text{P})$ is largely forbidden. Since the allowed $A^2\Delta - X^2\Pi$ transition of SiH is forbidden in the limit of the separated atom, the large dependence of the electronic transition moment upon the internuclear distance is understandable.

To confirm the strong r dependence of the SiH transition moment of the $A^2\Delta - X^2\Pi$ system, we compare the observed fluorescence lifetimes, τ_f , from the upper vibronic levels with calculated transition probability, A . The fluorescence lifetime is related with the transition probability by

Table 4 Calculated transition moments of the $A^2\Delta - X^2\Pi$ transition of SiH calculated by the r -centroids approximation and numerical integration.

v''/v'	0	1	2	3	4	5
0	2.6552(-1)	5.5566(-3)	0.0000	1.2686(-6)	0.0000	1.6914(-6)
	2.6657(-1)	5.7965(-2)	7.5452(-3)	3.0454(-4)	2.6773(-4)	6.5245(-4)
1	5.0958(-4)	2.2788(-1)	2.9795(-2)	1.1800(-3)	0.0000	0.0000
	6.1737(-3)	2.3745(-1)	1.0735(-1)	3.3748(-2)	9.2876(-3)	2.7581(-3)
2	3.0730(-4)	5.2057(-3)	1.5653(-1)	6.8224(-2)	1.2854(-2)	1.7779(-3)
	6.7715(-3)	1.6066(-2)	1.8930(-1)	1.4333(-1)	7.5056(-2)	3.5767(-2)
3	1.6300(-5)	1.3384(-3)	1.7527(-2)	6.5005(-2)	8.2151(-2)	3.9100(-2)
	1.2851(-3)	1.1368(-2)	4.0675(-2)	1.1918(-1)	1.4339(-1)	1.0906(-1)
4	1.7519(-6)	1.5210(-4)	4.3302(-3)	2.7723(-2)	5.1163(-3)	4.0178(-2)
	1.1679(-3)	3.7244(-3)	1.8160(-2)	5.3856(-2)	3.9583(-2)	9.4005(-2)
5	2.0048(-6)	0.0000	8.9428(-4)	1.0675(-2)	1.8151(-2)	5.1989(-3)
	8.8315(-4)	1.8046(-3)	7.7897(-3)	2.6400(-2)	4.6011(-2)	1.9083(-2)

The transition moment at the r centroid more than 3.5 Å is set to zero, because this exceeds the computational range. Since at a nuclear distance more than 3.5 Å, the predicted transition moment is equal to zero, this procedure is reasonable.

$$1/\tau_f = A_{v'} = \sum_{v''} A_{v'v''} \quad (8)$$

The transition probability, A , can be expressed as

$$A_{v'} = \frac{64\pi^4}{3h} \sum_{v''} \nu_{v'v''}^3 \langle v' | R_e(r) | v'' \rangle^2 \\ = 2.026 \times 10^{-6} \sum_{v''} \nu_{v'v''}^3 \langle v' | R_e(r) | v'' \rangle^2, \quad (9)$$

where $\nu_{v'v''}$ is the transition energy between the upper v' and lower v'' levels. The constant, 2.026×10^{-6} , is the product of A in s^{-1} , $\nu_{v'v''}$ in cm^{-1} , and $R_e(r)$ in atomic units. Since the observed LIF from the upper vibronic levels are terminated to several vibronic levels of the ground state, $A_{v'v''}$ is summed over all v'' states. Under the F-C approximation, the nuclear distance dependence of the transition moment is ignored, and then the observed lifetimes have the following relation with the F-C factors using Eqn. (1):

$$1/\tau_f = 2.026 \times 10^{-6} R_e^2 \sum_{v''} \nu_{v'v''}^3 \langle v' | v'' \rangle^2. \quad (10)$$

Figure 3 shows the relation between $1/\tau_f$ and $\sum_{v''} \nu_{v'v''}^3 \langle v' | v'' \rangle^2$.

The fluorescence lifetimes from $v' = 0$ and 1 levels show a linear relation with $\sum_{v''} \nu_{v'v''}^3 \langle v' | v'' \rangle^2$, but $v' = 2$ largely deviates from the linear relation, because of a predissociation process in the $v' \geq 2$ of the $A^2\Pi$ state.^{15,21} From the slope of the linear relational line, the transition moment of the SiH, $A^2\Delta - X^2\Pi$ system is estimated to be 0.25 atomic units under the F-C approximation. The value is reasonable with respect to the mean value of that evaluated from *ab initio* computation²⁵) as shown in Fig.2.

Utilizing the r -centroid approximation, the transition probabilities are reduced to

$$1/\tau_f = 2.026 \times 10^{-6} \sum_{v''} R_e(\bar{r}_{v'v''})^2 \nu_{v'v''}^3 \langle v' | v'' \rangle^2. \quad (11)$$

Figure 4 represents the plots of the left and right sides of Eqn. (11), i.e. $1/\tau_f$ vs. $2.026 \times 10^{-6} \sum_{v''} R_e(\bar{r}_{v'v''})^2 \nu_{v'v''}^3 \langle v' | v'' \rangle^2$. The nearly proportional relation with an intercept at zero between them indicates appropriate evaluation of the transition moment

Fig.3 The plot of the inverse of the observed fluorescence

lifetimes vs. $\sum_{v''} v_{v''}^3 \langle v' | v'' \rangle^2$.

by the r -centroid approximation.

Assuming a linear expression for the square of the transition moment with the r -centroid, *i.e.* $R_e(\bar{r}_{v'v''})^2 = a_0 + a_1 \cdot \bar{r}_{v'v''}$,¹⁵⁾ we can obtain the transition moment under the r -centroid approximation with only the F-C factors using the following equation;

$$1/\tau_f = 2.026 \times 10^{-6} \sum_{v''} (a_0 + a_1 \cdot \bar{r}_{v'v''}) v_{v''}^3 \langle v' | v'' \rangle^2, \quad (12)$$

From the analysis of this equation using the τ_f of the $v' = 0$ and 1 levels, the square of R_e is estimated to be

$$R_e(\bar{r}_{v'v''})^2 = 0.2943 - 0.1507 \cdot \bar{r}_{v'v''} \quad (13)$$

The transition moments for the vibronic bands calculated from a_0 , a_1 and $\bar{r}$ are comparable to the *ab initio* values. It is also shown that the transition moment varies inversely with the internuclear distance.

Figure 4 also shows the relation of Eqn. (9) with the numerically calculated transition moments. The relation is almost proportional as well, thus the quantitative validity of the *ab initio* transition moment²⁵⁾ was confirmed with the observed fluorescence lifetimes.

Summary

In this work, the LIF excitation spectra of the $A^2\Delta - X^2\Pi$ transition of SiH and the time profiles of the LIF from the vibronic levels of the A state have been measured in supersonic free expansions. On the basis of the observed intensity distribution of the vibronic bands and the fluorescence lifetimes, we discussed the strong dependence of the transition moment of the SiH, A - X system on the internuclear distance. The evaluation procedure of the transition moment described in this work facilitates quantitative estimation of the concentration of reaction intermediates from spectroscopic information observed under manufacturing processes such as, CVD and CBE; *i.e.* it is possible to estimate the reliable concentration from the analysis of the spectroscopic data using the F-C factors derived from simple calculation and the electronic transition moment evaluated by the fluorescence lifetime experimentally or obtained by the familiar *ab initio* computation theoretically.

Fig.4 The plots of the inverse of the observed fluorescence

lifetimes vs. $2.026 \times 10^{-6} \sum_{v''} v_{v''}^3 \langle v' | R_e(r) | v'' \rangle^2$ (circles) and $2.026 \times 10^{-6} \sum_{v''} R_e(\bar{r}_{v'v''})^2 v_{v''}^3 \langle v' | v'' \rangle^2$ (squares).

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