^{29}SiH$_4$ and ^{30}SiH$_4$: Dipole Moment Parameters of the ν_2/ν_4 Dyad from Stark Effect Observations with Laser Sidebands

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The linear Stark effect within the ν_2/ν_4 dyad of ^{29}SiH$_4$ and ^{30}SiH$_4$ has been investigated by applying the infrared sideband technique at microwave modulation frequencies. Two vibration-induced dipole moment parameters have been measured for each isotopomer on natural abundance samples. © 1990 Academic Press, Inc.

1. INTRODUCTION

The dipole moment and the pure rotational spectrum of the regular isotopomer of silane have been the subject of several investigations (*1–11*). So far, efforts to measure the dipole moment have been mainly concentrated on the vibrational ground state, where the dipole moment arises from centrifugal effects only. This centrifugal distortion moment θ_z^{xy} had been estimated from FIR line strength (*1*) and subsequently determined from resolved M components of pure rotational transitions observed in a microwave Stark spectrometer (*5*). The second-order Stark effect in the ground state has been observed with infrared–radiofrequency double resonance and with laser Stark spectroscopy (*7*). Attempts to observe the linear effect in either the ground or the excited state with these two techniques were unsuccessful because no near coincidences with suitable molecular transitions (*E*-type) and the fixed-frequency laser lines (CO$_2$ or N$_2$O) could be found.

According to Mizushima and Venkateswarlu (*12*), a dipole moment can occur in vibrationally excited states when certain symmetry requirements are fulfilled. For tetrahedral molecules this effect occurs in vibrational modes with threefold degeneracy (*13*). Although the vibration-induced dipole moment is in general larger than the centrifugal distortion moment (*10*), there are two problems involved in its determination from the Stark effect. As only the linear effect exhibits sufficient splitting of excited state levels, one has to rely on the few E-type transitions (among the A- and F-type ones). Secondly, until recently no suitable theoretical model existed to calculate the Stark coefficients for molecules belonging to this symmetry group, especially when the effects of strong vibrational interaction between the ν_4 and the ν_2 fundamentals in SiH$_4$ are present (*14*).

The development of tunable infrared spectroscopy using modulation sidebands at microwave frequencies allowed the resolution of the linear Stark effect using saturation spectroscopy. This technique permits the determination of the IR frequencies with an accuracy comparable to that of pure rotational spectroscopy (15). Dipole moment measurements in the ν_2/ν_4 excited state with tunable laser sidebands were performed by Frye et al. (10) and, recently, by Prinz et al. (11) on the regular species of silane.

Based on the well-known Hamiltonian of the ν_2/ν_4 dyad of the molecule (16–20), M. Loëte gave the complete dipole moment development (21) and applied it to the regular species of silane, ^{28}SiH$_4$, as well as to ^{13}CD$_4$ (11).

Since the natural abundances of ^{29}SiH$_4$ and ^{30}SiH$_4$ are 4.70% and 3.09%, respectively, it seemed promising to look for isotope transitions in order to determine the dipole moment parameters from the linear Stark effect in the same way as for the regular species (11).

2. EXPERIMENTAL DETAILS

The spectrometer suitable for observation of saturation dips has been described already (11, 15). The modulation sidebands are tunable between 12 and 18 GHz on either side of CO$_2$ laser lines. The laser was stabilized on the fluorescence emission Lamb dip and could also be operated with ^{13}CO$_2$ or C^{18}O$_2$. Sideband power was of the order of a few mW, depending somewhat on the MW modulation frequency, resolution $\approx$600 kHz. The absolute accuracy of frequency measurement was found to be <200 kHz from a comparison of our frequencies obtained for a few SiF$_4$ lines with the result obtained at the Technical University of Vienna (22). Reproducibility of a particular transition frequency with our apparatus was 20 kHz or better. A 1.2-m J-band waveguide served as sample cell. It was equipped with a Stark septum leaving a gap of 7.65 mm. Imperfections in the field homogeneity introduced additional line broadening of the M-components. Square wave Stark modulation at 35 kHz was applied; a DC field up to 4500 V cm^{-1} was used. In order to determine the position of the unsplit line independently, measurements with frequency modulation (60–80 kHz) were performed. Usually 10 sweeps (3.4 sec sweep time each at a time constant of 4 or 12.5 msec) were averaged. Laser polarization could be chosen parallel or perpendicular with respect to the Stark field.

A peculiarity of saturation spectroscopy which should be mentioned is that the saturation dip intensity is a nonlinear function of the pressure. It peaks within a narrow pressure range and decreases toward higher pressure because of relaxation effects. This optimum pressure varies considerably for the isotopomers with different abundances in a natural gas mixture. For the species under investigation a higher sample pressure (20–30 μbar) had to be chosen compared with observations on the main isotope (10 μbar). The sample was purchased from Matheson and used without further purification.

3. THEORY

The theoretical treatment has been given by Loëte (11, 21). The threefold degenerate vibration ν_4 is coupled to the twofold degenerate ν_2 via Coriolis interaction. In this dyad the wave functions are mixed to different extent. The effective Hamiltonian of this dyad is built up from vibrational and rotational tetrahedral tensor operators.

TABLE I

$^{29}SiH_4$ $\Delta M = 0$ Transitions

Transition	M'	Field (V/cm)	Stark Splitting (MHz)	Reduced Splitting (MHz·cm/kV·M')
R4 1E 1	4	3870	8.46	0.219(35)
R7 1E 1	5	3857	9.59	0.256(31)
Q10 2E 3	10	2059	7.54	0.366(-)[*]

The ground state and the effective dipole moment in the v_2/v_4 dyad can be written in a similar way, where we consider only the first order development. To this approximation one has to take into account one contribution in the ground state and three in the excited state. We have

$$^{GS}\mu^{(F_2)} = \mu_0 \mathbb{R}^{2(2,F_2)}$$

$$^{D}\mu^{(F_2)} = \mu_0 \mathbb{R}^{2(2,F_2)} + \mu_{44}{}^{+1}\mathbb{V}_{4,4}^{F_2 F_2 (F_2)} + \mu_{24}{}^{+1}\mathbb{V}_{2,4}^{EF_2(F_2)}.$$

These developments have been used already to calculate the rotational spectra of CH_4, CD_4, and SiH_4 (23–25, 9).

The ground state expression and the first term in the dyad dipole moment development describe the centrifugal effect (26). The second term means the effect of the vibration-induced dipole moment (Mizushima–Venkateswarlu effect) in an isolated threefold degenerate vibration, while the last term follows from the vibration interaction.

For relations between different dipole moment parameters chosen by Mills et al. (13), Frye (10), and Watson (26), see Ref. (11).

TABLE II

$^{30}SiH_4$ $\Delta M = 0$ Transitions

Transition	M'	Field (V/cm)	Stark Splitting (MHz)	Reduced Splitting (MHz·cm/kV·M')
Q2 1E 1	2	3216	12.85	2.01(3)
Q4 1E 1	4	3981	15.41	0.968(14)
Q5 1E 2	5	3987	12.42	0.623(24)
Q9 1E 3	9	2974	3.76	0.138(-)[*]
R4 1E 1	4	3530	7.62	0.525(14)
R5 1E 1	4	3758	6.19	0.391(31)
R7 1E 1	5	3810	9.50	0.436(55)
P8 1E 4	7	2773	1.69	0.068(-)[*]

M' refers to the highest Stark component used in the fit.

[*] Unresolved Stark effect; but due to the intensity relations the extension of the multiplet on the frequency scale is clearly recognizable.

TABLE III

^{29}SiH$_4$ $\Delta M = \pm 1$ Transitions

Transition		$\pm M''$	$\pm M'$	Field (V/cm)	Stark Splitting (MHz)	Reduced Splitting (MHz·cm/kV)
R4	1E 1	4	5	3804	9.69	2.53(5)
R6	1E 1	6	7	4100	4.24	1.03(15) *
R7	1E 1	7	8	4366	15.79	3.67(3)
R10	2E 1	10	11	2856	12.77	4.47(10) *
R11	2E 1	11	12	3200	13.14	4.10(20) *
R12	2E 1	12	13	3426	6.52	1.90(15) *
R16	3E 1	16	15	1260	7.68	6.10(10) *

The linear Stark shift of E-level M components is calculated from the dipole moment matrix on the basis of the zero-field eigenfunctions. The linear Stark shifts in the ground and excited (dyad) states can be expressed in the forms

$$^{GS}\Delta E(J, \alpha) = \mathcal{E} M \mu_0{}^{GS} C_0(J, \alpha)$$

$$^{D}\Delta E(J, \alpha) = \mathcal{E} M(\mu_0{}^{D} C_0(J, \alpha) + \mu_{44}{}^{D} C_{44}(J, \alpha) + \mu_{24}{}^{D} C_{24}(J, \alpha))$$

with the Stark coefficients C and the field strength $\mathcal{E}$.

TABLE IV

^{30}SiH$_4$ $\Delta M = \pm 1$ Transitions

Transition		$\pm M''$	$\pm M'$	Field (V/cm)	Stark Splitting (MHz)	Reduced Splitting (MHz·cm/kV)
Q2	1E 1	1	2	1026	4.20	4.15(13)
		0 2	1 1	1026	2.05	2.01(8)**
Q4	1E 1	3	4	2811	11.65	4.15(6)
Q5	1E 2	5 3	4 4	2883	6.63	2.41(12)
R4	1E 1	4	5	4302	10.98	2.53(7)
R6	1E 1	6	7	3200	3.51	1.10(20)
R7	1E 1	7	8	4118	14.75	3.56(5)
R11	1E 2	11	12	3700	5.83	1.58(20) *
R13	2E 1	13	14	2973	15.36	5.17(20) *
P8	2E 3	4	5	3961	3.28	0.83(10) *
P8	1E 4	6	7	2773	1.69	0.68(-) *

M'',M' refers to the energy level in the ground and in the
    upper state respectively.
  * Unresolved Stark effect; but due to the intensity relations
    the extension of the multiplet on the frequency scale is
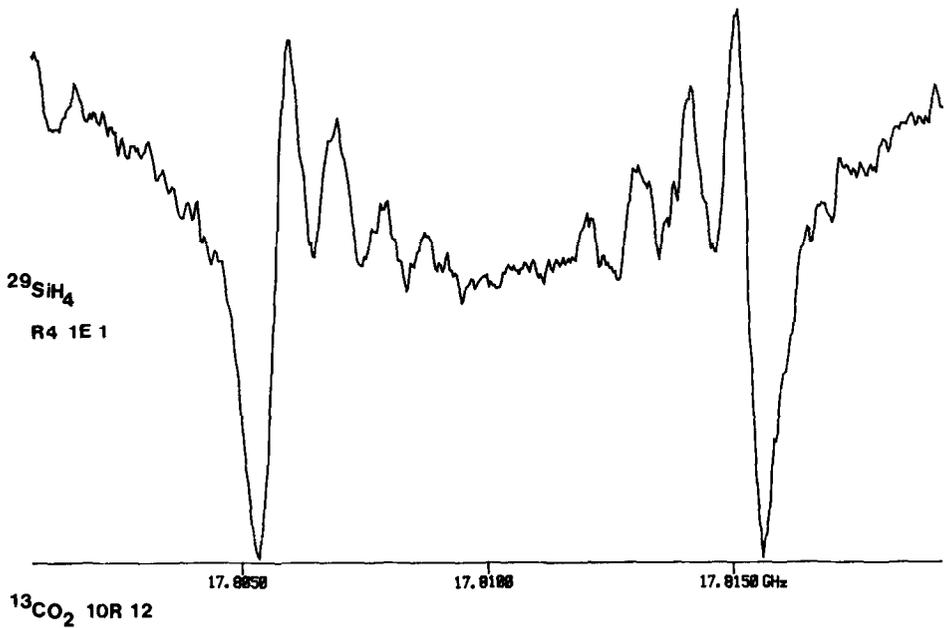   clearly recognizable.
 ** not used in the fit.

FIG. 1. The transition $R4\ 1E\ 1$ at 922.517 234(7) cm^{-1} in the ν_2/ν_4 diad of ^{29}SiH$_4$. Selection rule is ΔM = ±1. The splitting achieved with a field of 4.063 kV · cm^{-1} is almost entirely due to the vibration-induced dipole moment in the excited state. The upper sideband of the $10R\ 12$ line of the ^{13}CO$_2$ laser (not stabilized) was scanned over 27.62 MHz. Field modulation (250 V$_{pp}$ · cm^{-1}) at 50 kHz was applied.

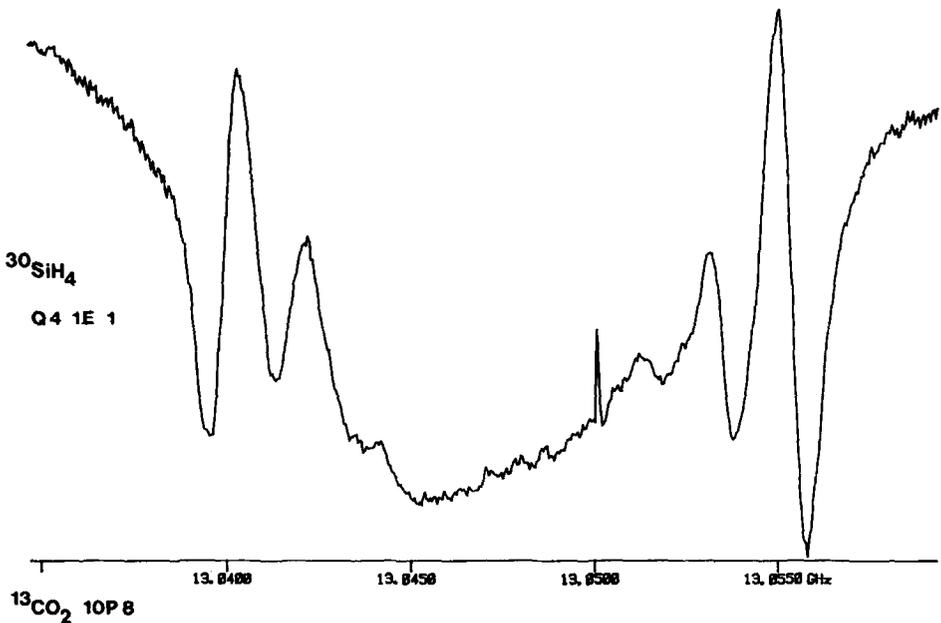FIG. 2. $\Delta M = 0$ satellites of $Q4\ 1E\ 1$ (^{30}SiH$_4$) at a field strength of 3079 V · cm^{-1}. The $10P8$ line of the ^{13}CO$_2$ laser was used as carrier frequency. Laser stabilized, 10 recordings averaged.

^{30}SiH$_4$

R7 1E 1

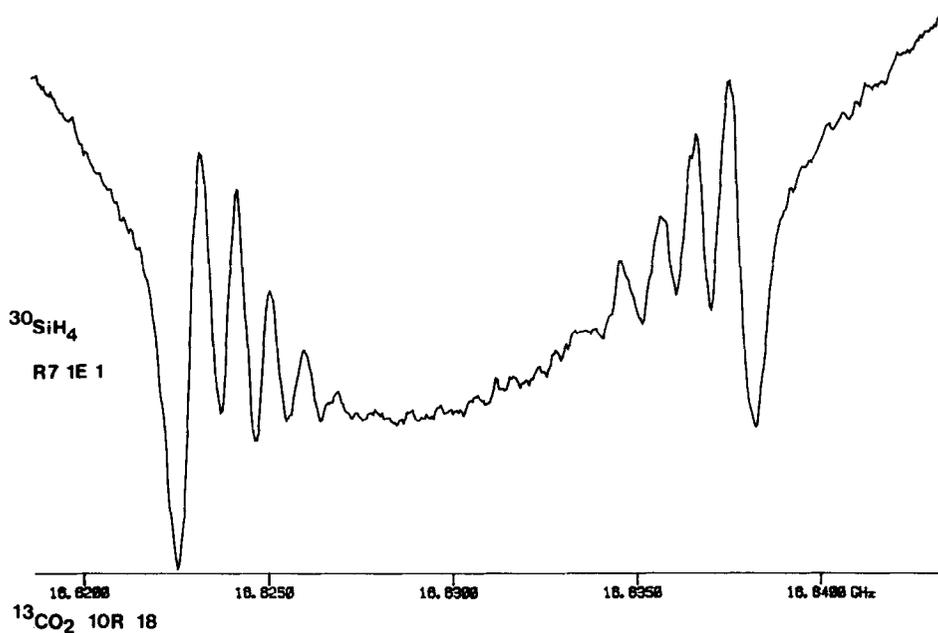|				
16.8200	16.8250	16.8300	16.8350	16.8400 GHz

^{13}CO$_2$ 10R 18

FIG. 3. $\Delta M = \pm 1$ Stark spectrum of the ^{30}SiH$_4$ transition $R7$ $1E$ 1, recorded with the upper sideband of the 10R 18 laser line of ^{13}CO$_2$. Ten recordings averaged. Field: 4118 V $\cdot$ cm^{-1}.
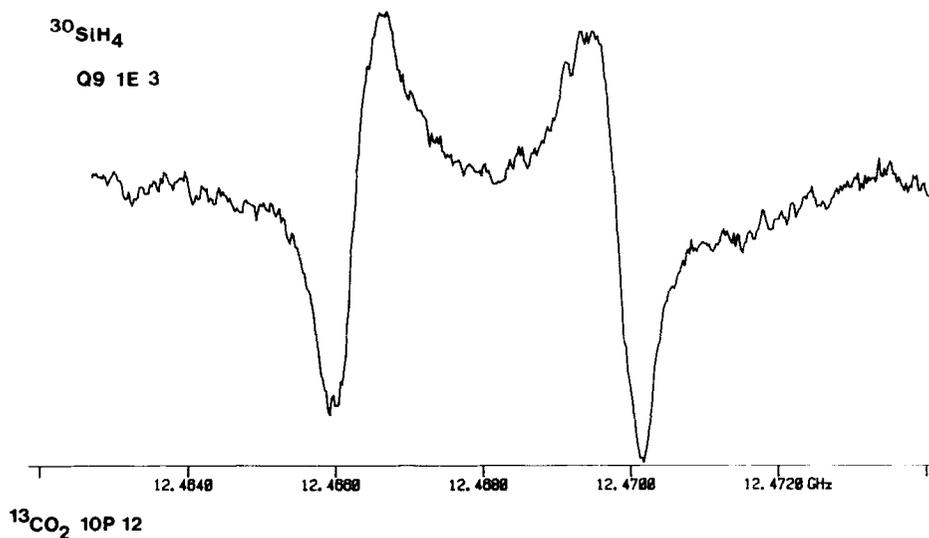

^{30}SiH$_4$

Q9 1E 3

12.4840	12.4660	12.4680	12.4700	12.4720 GHz

^{13}CO$_2$ 10P 12

FIG. 4. $Q9$ $1E$ 3 [903.333 849(7) cm^{-1}; $\Delta M = 0$] of ^{30}SiH$_4$, recorded at a field of 2.974 kV $\cdot$ cm^{-1}; 10 scans averaged. Although single satellites are not resolved the splitting of the outermost components (M' = 9 $\leftarrow$ M'' = 9) can be determined fairly accurately.

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TABLE V

Dipole Moment Parameters of the ν_2/ν_4 Dyad of the Natural Silane Isotopomers

	fixed	this work[a]			
	$\mu_0 \cdot 10^5$ D	$\mu_{24} \cdot 10^2$ D	$\mu_{44} \cdot 10^2$ D	$\theta_z^{xy} \cdot 10^5$ D	$P \cdot 10^3$ D
^{29}SiH$_4$: 1.325(17)		3.15(84)	-0.77(21)	3.75(5)	3.1 (9)
^{30}SiH$_4$: 1.325(17)		2.409(27)	-1.240(41)	3.75(5)	5.06 (17)
^{28}SiH$_4$[b] : 1.325(17)		2.259(66)	-1.220(34)	3.75(5)	4.98(14)

a) fitted with μ_0 fixed to our recent experimental value (ref.28)
b) experimental data from ref.11 plus recent measurements

4. OBSERVATION

The Stark effect has been observed in a total of 10 transitions of ^{29}SiH$_4$ and 18 transitions of ^{30}SiH$_4$; resolution of single M components was achieved with two and with six transitions, respectively. Tables I to IV give the splitting observed and the field strength applied. From the transition matrix elements the high-M components in the Q-branch show strong intensity when the Stark field is parallel to the laser polarization (selection rule $\Delta M = 0$) while in the P and R branches the low-M satellite was saturated more easily. For the case $\Delta M = \pm 1$ (field perpendicular) the intensity relations are the other way round (i.e., strong high-M satellites in the P and R branches). Therefore, one could determine the positions of the outermost components quite accurately even in the case of an unresolved effect for Q-branch (parallel) or P- and R-branch (perpendicular) transitions.

Figure 1 shows a fairly strong transition $R4\ 1\,E\ 1$ at $922.517\ 234(7)\ \text{cm}^{-1}$ of ^{29}SiH$_4$ ($\Delta m = \pm 1$). Because of the low splitting in the vibrational ground state, the observed pattern is almost entirely due to the vibration-induced dipole moment in the ν_2/ν_4 dyad.

Figure 2 gives an example of a parallel Q-branch line ($Q4\ 1\,E\ 1$ at $906.617\ 620(7)$ cm^{-1}) and Fig. 3 a perpendicular R-branch transition ($R7\ 1\,E\ 1$ at $927.855\ 049(7)$ cm^{-1}), both of ^{30}SiH$_4$. In contrast, the transition $Q9\ 1\,E\ 3$ ($903.333\ 849(7)$ cm^{-1}; $\Delta M = 0$) could not be resolved even at the highest field which could be used at this sample pressure (≈ 2979 V cm^{-1}, Fig. 4).

Due to $1\,f$ detection, the line shape is a first derivative for Stark (≈ 30 kHz) as well as for frequency ($\leqslant 100$ kHz) modulation.

5. ANALYSIS AND RESULTS

In order to determine the dipole moment parameters the Stark coefficients $^{D}C_0$, $^{D}C_{44}$, and $^{D}C_{24}$ were calculated by the procedure described by Loëte (11). The C-values have been calculated taking the eigenvectors from Ref. (27).

Parameters have been fitted using an unweighted least-squares procedure (Table V). As the contribution of the centrifugal distortion term is small compared to the experimental precision, the μ_0 parameter cannot be determined accurately. This parameter was fixed for both isotopes to the value determined for ^{28}SiH$_4$ from (IR–IR) double resonance observations (28). This value is very close to the value determined by Kagann et al. (6). Using the value given by Prinz (29) one obtains similar results (within the standard deviation) for the parameters.

For ^{29}SiH$_4$ the majority of the observed E type transitions belong to the R branch, while for ^{30}SiH$_4$ and ^{28}SiH$_4$ (11) lines come from all three branches, thus contributing evenly to the result. There are only two resolved ^{29}SiH$_4$ lines, therefore the parameters are highly correlated and deviate slightly from the ^{28}SiH$_4$ values. For this reason we have given three times the standard deviation for the 29 species.

As expected, μ_{44} and μ_{24} for ^{30}SiH$_4$ are the same as for ^{28}SiH$_4$ (within the standard deviation).

6. CONCLUSION

The infrared spectra of ^{29}SiH$_4$ and ^{30}SiH$_4$ have been investigated in order to resolve the linear Stark effect due to the vibration-induced dipole moment in the ν_2/ν_4 dyad. This was achieved by applying the saturation technique using tunable CO_2 laser sidebands at microwave modulation frequencies. With the theory, developed by Loëte (21, 11), the two dipole moment parameters μ_{44} and μ_{24} could be determined for each of the isotopomers.

7. ACKNOWLEDGMENTS

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