

Tunable Laser Diode Study of the ν_3 Band of SiF₄ near 9.7 μm ¹

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Doppler-limited tunable-diode laser spectra of the stretching fundamental ν_3 of ²⁸SiF₄ near 1031 cm^{-1} were analyzed and the spectroscopic constants determined. The ν_3 vibrational dipole moment derivative was determined for several rovibrational lines.

INTRODUCTION

The ν_3 mode of SiF₄ has stimulated recent interest since multiple-photon dissociation occurs when this mode is pumped by a high-power 9.4- μm CO₂ laser (1). The various experiments involving pumping the ν_3 band of SiF₄ with a CO₂ laser include saturation spectroscopy (2-4), photon echoes (5, 6), laser-induced fluorescence and dissociation (7-10), and silicon isotope separation (11). A full understanding of these effects depends on the identification of the detailed rovibrational structure of SiF₄ that is nearly resonant with CO₂ laser frequencies (12). Such information is not extractable from the previous low-resolution band-contour studies of the ν_3 band (13-16).

We report here a high-resolution Doppler-limited analysis of the ν_3 band of ²⁸SiF₄ between 1023 and 1038 cm^{-1} . This is the first step necessary for an understanding of the ν_3 vibrational ladder and the multiple-photon absorption process. We have assigned most ground-state transitions in the above range corresponding to *R*(60)-*P*(60). A total of 215 of the assigned transitions were used in a least-squares fit to a 10-parameter model Hamiltonian, giving an overall standard deviation of $6 \times 10^{-4} \text{cm}^{-1}$. For several lines in the *R* branch, where our instrumental resolution was sub-Doppler, we have determined the vibrational transition dipole from intensity measurements.

EXPERIMENTAL DETAILS

The ν_3 band of SiF₄ was recorded using Pb_{1-x}Sn_xTe semiconductor diode lasers in spectrometers whose characteristics have been described previously (17-20). The

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sample was cooled to 170–200 K to suppress hot-band structure. The frequencies of lines used in the fit of the spectroscopic constants were measured using a double-beam system (19) in which the SiF₄ spectrum and that of a calibrating gas were recorded simultaneously. Immediately before or after each such run, interference fringes from a germanium etalon (free spectral range 0.0165 cm⁻¹) were recorded to establish the diode tuning rate. All lines selected for measurement were within ± 0.1 cm⁻¹ of a calibration feature of CO₂ (21) or OCS (17). Repeated determinations of the frequencies of several lines indicated that the measurements are accurate to within ± 0.001 cm⁻¹. For the determination of the transition dipole moment, SiF₄ pressures were measured using a capacitance manometer to better than 5%.

ASSIGNMENTS AND ANALYSIS

The transition frequencies in a dipole-active fundamental of a spherical-top molecule can be expressed in the diagonal approximation as (22–24)

P branch:

$$\nu_P(J, C^n) = m - nJ + pJ^2 - qJ^3 + sJ^4 + [g + hJ + kJ^2]\bar{F}(4) + z'\bar{F}(6), \quad (1a)$$

Q branch:

$$\nu_Q(J, C^n) = m + vJ(J + 1) + wJ^2(J + 1)^2 + [-2g + uJ(J + 1)]\bar{F}(4) - 2z'\bar{F}(6), \quad (1b)$$

R branch:

$$\nu_R(J, C^n) = m + n(J + 1) + p(J + 1)^2 + q(J + 1)^3 + s(J + 1)^4 + [g - h(J + 1) + k(J + 1)^2]\bar{F}(4) + z'\bar{F}(6), \quad (1c)$$

with the off-diagonal terms in the Coriolis submatrices neglected. The index *C* designates the tetrahedral species with counting index *n* for repeated species within each ground state angular momentum *J*. The $\bar{F}(4)$ and $\bar{F}(6)$ are products of symmetry-adapted fourth- and sixth-rank tensor coefficients. These have been calculated by Krohn (25) for all *Cⁿ* up to *J* = 150.

These formulas were sufficient for making line assignments in the *P*, *Q*, and *R* branches for *J* ≤ 40. However, for assigning lines corresponding to higher-*J* transitions it was necessary to include the off-diagonal Coriolis submatrices and calculate the “off-diagonal corrections” (26). To calculate these corrections, we diagonalized the full Coriolis energy matrix for each *J'* of ν_3 . For this purpose it was necessary to add the appropriate ground-state energies

$$E_0 = B_0J(J + 1) \quad (2)$$

to the transition frequencies in Eq. (1) before diagonalizing, where

$$J' = \begin{cases} J - 1 & P \text{ branch} \\ J & Q \text{ branch} \\ J + 1 & R \text{ branch.} \end{cases} \quad (3)$$

One may then define the ν_3 scalar parameters from the spectroscopic parameters of Eqs. (1) to be

$$m \sim \nu_3 - 2(B\zeta_3), \quad (4a)$$

$$n \sim B_3 + B_0 - 2(B\zeta_3), \quad (4b)$$

$$Z_{3s} \sim p - v, \quad (4c)$$

$$Y_3 = B_3 - B_0 \sim (v + 2p)/3. \quad (4d)$$

The ν_3 scalar energies for each J' then become

$$E_P = \nu_3 + 2(B\zeta_3)J' + B_3J'(J' + 1) - Z_{3s}(J' + 1)^2/3 - q(J' + 1)^3 + s(J' + 1)^4, \quad (5a)$$

$$E_Q = \nu_3 - 2(B\zeta_3) + B_3J'(J' + 1) + 2Z_{3s}J'(J' + 1)/3 + w(J')^2(J' + 1)^2, \quad (5b)$$

$$E_R = \nu_3 - 2(B\zeta_3)(J' + 1) + B_3J'(J' + 1) - Z_{3s}(J')^2/3 + q(J')^3 + s(J')^4. \quad (5c)$$

Including the tensor terms in the ν_3 matrix for a given J' along with the above scalar terms and diagonalizing results in the ν_3 rovibrational energies. Subtracting the ground-state energies gives us accurate transition frequencies. For the accuracy needed, it was not necessary to include the quartic scalar term $D_0J^2(J + 1)^2$ explicitly in the ground-state energy although it is implicit in the spectroscopic parameters q , s , and w .

In order to least-squares fit the calculated transition frequencies to the data, it is necessary to determine the derivative of the ν_3 matrix eigenvalues (energies) with respect to each parameter. Although in most cases the diagonal terms in the matrix can be taken, it is sometimes necessary to use the expectation value in the energy eigenbasis according to the Feynman-Hellman theorem. From this latter procedure we were able to fit $B\zeta_3$ due to the dependence of the off-diagonal corrections on this parameter.

Complete assignments were made from $R(60)$ to $P(60)$ in the range 1023–1038 cm^{-1} for which we had continuous diode coverage. We used 215 lines in the fit which were usually unblended and were always within $\pm 0.1 \text{ cm}^{-1}$ of a CO_2 or OCS calibration feature. In cases where a line consisted of an unresolved cluster of several transitions, only one member was used in the fit. This member corresponded to that closest to the spin statistically weighted center of gravity when blending was significant. Included among the 215 lines are lines identified in the $^{12}\text{C}^{16}\text{O}_2$ saturation spectra (12) taken with a waveguide laser (27).

In Table I are listed the rovibrational transitions used in the fit along with their measured frequencies. A fit to the data in Table I using Eqs. (1), (2), and (5) resulted in the determination of the 10 spectroscopic constants listed in Table II. The constants u and z' were too small to be determined. Also listed in Table II are constants derived according to Eqs. (4).

The Coriolis constant $B\zeta_3$ was fixed at a value consistent with Eq. (4b) when the value for $B \sim B_3 \sim B_0 = 0.13814(36) \text{ cm}^{-1}$ was derived from electron diffraction data (28). Since the constant n is very well determined, the error for $B\zeta_3$ is basically

TABLE I
Observed and Calculated Transition Wavenumbers in ν_3 of ²⁸SiF₄

Line	C	n ^a	$\nu_{\text{obs}}, \text{cm}^{-1}$	Δ^b	Line	C	n ^a	$\nu_{\text{obs}}, \text{cm}^{-1}$	Δ^b	Line	C	n ^a	$\nu_{\text{obs}}, \text{cm}^{-1}$	Δ^b
P(59)	F1	3*	1023.1605	-16	P(32)	F1	2	1027.008	1	Q(23)	F1	1*	1031.163	5
	A1	0*	.2175	-9		F2	2	.0105	2	Q(22)	A2	1*	.1015	2
P(58)	A1	3*	.2105	-12		A2	0	.0145	-3		F1	4*	.149	4
	F1	10*	.258	-4		F2	3	.021	3		A1	1*	.1855	4
P(57)	F1	10	.1645	-10	P(30)	A1	1	.3095	-8	Q(20)	A1	1*	.1545	10
	F2	9	.172	-11		F1	3	.317	-2		F1	1*	1032.153	6
	F1	9	.1855	-4		F2	3	.319	-1	R(5)	F1	0	.155	-1
	E	5	.196	-10		A2	1*	.3335	3		F2	0	.155	6
	A2	2	.2035	-4		F1	4*	.3535	-8	R(7)	A2	0	.4025	7
	F1	8	.2225	-9		A1	2*	.3785	-8	R(8)	F1	0*	.524	5
	A1	2*	.250	2	P(28)	A2	1*	.654	-7		A1	0*	.530	2
P(56)	F1	2*	.2655	2		F1	5*	.6815	-3	R(11)	E	1*	.886	3
P(54)	A1	4*	1024.0005	2	P(15)	F1	2*	1029.4145	0		F1	1	.8895	-1
	F1	12*	.0595	6		A2	0*	.433	7		A2	0*	.894	-1
	A2	4*	.123	13		F1	0*	.4485	7		F1	0*	.9015	-2
P(53)	A1	1*	1023.997	0	P(13)	E	1*	.680	-7	R(14)	E	0*	1033.2435	3
	A2	0*	1024.0915	8		A2	0	.686	-2		F2	1	.2485	0
P(52)	F1	7*	.0705	6		F2	1	.688	-4		A2	0*	.271	-4
	A2	2*	.1055	7		F1	2	.6895	-4	R(16)	E	0*	.478	-2
	F1	11*	.3425	-9		A1	0*	.697	1		A1	0	.4845 ^c	4
	A1	4*	.405	12		F1	0*	.7105	-4		F1	1	.4859 ^c	4
P(51)	E	6*	.080	5	Q(53)	E	8*	1030.756	7		F2	1	.4872 ^c	4
	A1	2	.115	8	Q(52)	F1	7*	.364	-13		A2	0	.4915 ^c	4
	F1	3*	.333	0	Q(51)	A1	1*	.4125	-1		F2	2*	.493	5
	A1	0*	.380	5		E	7*	.7245	-2		F1	2*	.502	-1
	F1	1*	.431	7	Q(49)	A1	1*	.3795	2		A1	1*	.517	5
P(50)	F1	6*	.369	9		F1	5*	.4455	0	R(32)	A1	2*	1035.438	6
	F1	8*	.4385	12	Q(48)	A1	3*	.354	-6	R(33)	F1	6	.3985	-2
P(49)	E	7*	.319	-7		F1	7*	.428	5		A2	1	.4075	-3
	A1	3*	.364	6	Q(47)	A2	1*	.4755	10		F2	4	.412	-2
	F1	9	.428	11	Q(46)	F2	2	.785	5		F1	5	.414	-3
	F2	8	.4325	11	Q(45)	A2	0*	.424	-1		F1	3*	.4425	2
	A2	2	.4465	20		A1	2	.752	-4	R(34)	A2	0	.463	0
	F2	7	.451	16	Q(44)	A2	2*	.3905	6		F2	0	.4687 ^c	-5
	F1	8	.455	18		F1	8*	.473	7		E	0	.4687 ^c	-6
P(46)	A2	3*	1025.2435	-9		F2	4	.766	-3	R(35)	F1	0*	.789	-4
P(45)	A2	0*	.240	-2	Q(43)	A2	0*	.349	1	R(36)	A1	2*	.778	-3
	A1	0*	.332	6		F1	1*	.440	7	R(45)	A1	0*	1036.891	4
P(44)	F1	6*	.312	5		A1	1	.7465	-7	R(46)	F1	8*	.9135	-2
P(43)	E	6*	.277	-1	Q(41)	A1	0*	.4495	4	R(47)	A1	1*	.900	-5
	A1	2*	.315	6		A1	1*	.7295	-8		F1	4*	.9255	7
P(42)	F1	7*	.667	-3	Q(40)	A1	3*	.404	6	R(48)	E	0*	.894	-1
	A1	3*	.707	-1		F1	5*	.768	-5		E	1*	.921	2
P(41)	F1	7	.6705	-5	Q(39)	F1	3*	.7535	-8		A1	4*	1037.283	-5
	E	4	.673	1	Q(38)	A2	1*	.7925	0	R(49)	F2	1*	.286	-3
	F2	6	.6795	2	Q(37)	A2	0*	.774	-1	R(50)	F1	8*	.271	-6
	F1	6	.686	2	Q(36)	A2	2*	.7485	-14		A2	2*	.308	2
	F2	5	.6995	3		A1	0*	1031.090	5	R(51)	F1	8	.2445	-5
	A2	1	.7015	3	Q(35)	F1	1*	1030.7895	3		E	5	.246	-9
	F1	5*	.720	-3		F1	7*	.7595	-5		F2	8	.253	-6
P(40)	F1	7*	.9495	-14	Q(34)	F1	2	1031.032	-6		F1	7	.2585	-5
	F1	8*	1026.0295	-4	Q(33)	F1	0*	1030.7225	-12		A2	2	.274	0
P(39)	A2	2	1025.9725	-9		A1	0*	.7995	2		F1	6*	.2925	1
	F2	6	.976	-9		F1	6	1031.0605	-3		A1	1*	.3165	5
	F1	6	.979	-10	Q(32)	A1	2*	1030.764	-4	R(52)	A1	0*	.269	-6
	F1	5	.992	-6		A2	0	1031.0635	-3		E	1*	.2995	3
	A2	1*	1026.0335	-1	Q(31)	E	3	.094	5		F1	8*	.4825	2
	F1	3*	.0615	8	Q(30)	F1	3	.0835	2	R(53)	F1	9	.4341 ^c	2
P(38)	E	0*	.0555	4	Q(29)	A2	1	.1325	0		E	5	.4385	3
	F1	8*	.3065	-12	Q(28)	A2	1*	.0295	3		F2	8	.441	4
	A2	2*	.351	-5		A1	1	.1035	5		F2	7	.455	8
P(37)	A2	1	.2875	-7		E	1	.1435	-1		F1	6*	.496	5
	F2	4	.299	-5	Q(27)	F2	1	.168	7	R(54)	E	0*	.453	-1
	F1	5	.3005	-6		A1	0*	.0985	-3		E	1*	.4845	4
	A1	1*	.320	-1		F2	3	.130	-2		A1	3*	.6555	1
	F1	3*	.345	-3	Q(26)	A1	1*	.184	-4	R(55)	A2	3	.6195	0
	A2	0*	.3745	0		F2	1	.1995	9		A1	2	.630	-1
P(36)	A1	0*	.3615	3		F2	1	.068	-5		F1	8	.638	5
	E	0*	.3915	6	Q(25)	A1	0*	.1385	-2		E	5	.6395	2
P(33)	A1	0*	.9975	-2	Q(24)	A2	1*	.1905	-5	R(56)	E	1*	.634	2
P(32)	E	1*	.9905	-1		A1	1							
	A1	0	1027.006	1										

^a An asterisk indicates that the transition shown is a member of a tight, unresolved cluster of several transitions.

^b $\Delta = (\nu_{\text{obs}} - \nu_{\text{calc}}) \times 10^4 \text{ cm}^{-1}$.

^c Frequency from saturation spectrum.

TABLE II
 ν_3 Spectroscopic Constants of $^{28}\text{SiF}_4^a$

Scalar constants:	Tensor constants:
$m = 1031.39661(13)$	$g = 4.1771(23) \times 10^{-5}$
$n = 0.127726(4)$	$h = 3.15(5) \times 10^{-8}$
$(B\zeta)_3 = 0.0743(4)^b$	$k = 1.28(13) \times 10^{-10}$
$p = -2.5489(20) \times 10^{-4}$	$u = z' = 0$
$v = -3.787(3) \times 10^{-4}$	Derived constants:
$q = -1.36(18) \times 10^{-8}$	$Z_{3S} \approx v - p$
$s = -1.10(6) \times 10^{-9}$	$= -1.238(3) \times 10^{-4}$
$w = 2.0(11) \times 10^{-10}$	$Y_3 \approx (v + 2p)/3$
	$= -2.962(2) \times 10^{-4}$

^a In cm^{-1} ; standard deviations, in parentheses, given in units of the last decimal place quoted.

^b Fixed; see text.

that of B_3 . This error in B_3 is also of the same magnitude as higher-order corrections to Eq. (4b). As described above, we were able to fit $B\zeta_3$ as a free parameter. We obtained the value

$$B\zeta_3 = 0.0777(16) \quad (6)$$

which is less accurately determined than the value obtained from electron diffraction, but in reasonable agreement.

Using the 10 spectroscopic constants in Table II, we have calculated all the $^{28}\text{SiF}_4$ ν_3 transition frequencies for $J' \leq 70$. A listing can be provided upon request. In Table I we compare the calculated frequencies with their measured values. The overall standard deviation is $6 \times 10^{-4} \text{ cm}^{-1}$ which should be compared with the Doppler width (FWHM) of $1 \times 10^{-3} \text{ cm}^{-1}$ at 200 K.

Because of the accuracy of our calculated frequencies, it is now possible to assign unambiguously the SiF_4 transitions seen in the $^{12}\text{C}^{16}\text{O}_2$ saturation spectra. Indeed, eight lines from the data mentioned above near the CO_2 $P(30)$, $P(32)$, and $P(34)$ lines were assigned to $R(53)$, $R(34)$, and $R(16)$ transitions, respectively. These eight lines are also listed in Table I and were included in our fit. All other transitions of $^{28}\text{SiF}_4$ from the vibrational ground state within $\pm 200 \text{ MHz}$ of CO_2 laser lines between 1023 and 1038 cm^{-1} are listed in another publication (12). From Table I one finds that the triplet reported by Harter *et al.* (2) near the CO_2 $P(32)$ line

is an $R(34) F_2^0 + E^0 + F_1^0$ cluster. They also report an $A_1 + F_1 + F_2 + A_2$ cluster nearby which belongs to an unassigned hot band.

Our calculations indicate the $P(36)$ line of CO₂ is between the $Q(1)$ and $R(0)$ lines of ²⁸SiF₄, detuned by 2.43 and 1.41 GHz, respectively. Thus multiple-photon absorption by ²⁸SiF₄ when pumped by the $P(36)$ CO₂ line can only originate from vibrational hot bands or multiphoton resonances to $2\nu_3$ or $3\nu_3$ disregarding power broadening effects. In the photon echo experiments with SiF₄, Gutman and Heer (5) correctly infer high- J R -branch absorption when pumping with 9.4- μm $P(30)$ to $P(34)$ lines of CO₂. Their lack of signal for $P(28)$ pumping is probably a result of the small rotational population for $J > 70$ giving rise to weak R -branch transitions. In the two-frequency experiments of Akulin *et al.* (9, 10), the $P(38)$ 9.4- μm CO₂ line was successfully used to pump SiF₄ near $P(15)$.

We hope that with the identifications made in the saturation spectra of ν_3 of SiF₄ a comprehensive effort to resolve the hyperfine structure can be undertaken similar to that achieved for SF₆ (29, 30). We note that in T_d symmetry with nuclear spin 1/2 the species of F_1^+ , F_2^- , A_1^- , A_2^+ , E^\pm have distinct inversion character (+ or -) and crossover resonances cannot arise from hyperfine mixing of species with different inversion character (31).

ν_3 TRANSITION DIPOLE MOMENT

From band strength measurements (32), the ν_3 transition dipole moment of SiF₄ has been calculated (33) to be $|\mu_3| = 0.276(14) D$. This dipole moment can also be determined from individual rovibrational line strengths according to the formula (33)

$$S_{if} = \frac{8\pi^3 N}{3hcZ} \nu_{if} \mu_3^2 \epsilon_i (2J' + 1) e^{-B_0 hc J(J+1)/kT} (1 - e^{-hc\nu_{if}/kT}). \quad (7)$$

Here N is the number of molecules per cm³, $Z = Z_V Z_R$ is the product of the vibrational and rotational partition functions, and ν_{if} is the wavenumber of the transition. The units in this equation are cm⁻² where μ_3 is in esu-cm ($1D = 1 \times 10^{-18}$ esu-cm). The nuclear-spin statistical weight is $\epsilon_i = 5, 2,$ and 3 for species $A, E,$ and F respectively. The rotational partition function is approximately (34)

$$Z_r = \frac{4}{3} \pi^{1/2} \left(\frac{B_0 hc}{kT} \right)^{-3/2} e^{B_0 hc/4kT}. \quad (8)$$

If the linewidth γ (FWHM) is Doppler-limited, we may relate the line strength to the peak height k_{if} by the standard relation

$$S_{if} = k_{if} \gamma_D \left(\frac{\pi}{4 \ln 2} \right)^{1/2}. \quad (9)$$

We have measured the peak heights of various rovibrational transitions in the R branch, where the diode was operating with sub-Doppler resolution. Peak height measurements were made in a pressure range of 0.7 to 20 Pa to minimize the pressure broadening. In this range the measured linewidths were always Doppler-limited which is consistent with the 19 nsec-Torr dephasing time (T_2) as measured

TABLE III
Dipole Transition Moments for Selected Rovibrational Lines of ν_3 of $^{28}\text{SiF}_4$

Line	T, K	Pressure, Pa	ν_{if} , cm^{-1}	$ \mu_3 $, Debye
R(18) F_1^1	296	0.7-4.0	1033.722	0.292
R(19) A_1^0	296	0.7-4.0	1033.839	0.308
R(20) F_1^2	296	0.7-20.0	1033.949	0.286
R(20) A_1^0	296	3.3-20.0	1033.955	0.327

by Gutman and Heer (5). The minimum pressure used was limited by the signal detection.

The peak heights were measured for at least three different pressures and the dipoles given for each line represent an average. As shown in Table III the calculated transition dipoles for the four lines measured are close to that calculated from the ν_3 band strength. The error in our $|\mu_3|$ is of the order of 10%, so the discrepancies between the $|\mu_3|$ of various lines may not be significant. Any hot band absorption, which should be prevalent in the room temperature measurements, would result in a value for $|\mu_3|$ too large. Our values for $|\mu_3|$ are consistently higher than the dipole moment reported previously but this value is within our experimental error. Our higher values confirm that the resolution of our instrument was indeed sub-Doppler.

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