

CO₂ laser coincidences with ν_3 of SiF₄ near 9.7 μm

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Doppler-limited tunable-diode laser spectra of the stretching fundamental (ν_3) of ²⁸SiF₄ at 1031 cm⁻¹ have been analyzed and the spectroscopic constants determined. Explicit identifications have been made for transitions near CO₂ laser lines between 1023 and 1038 cm⁻¹; 51 such transitions have been observed in sub-Doppler saturation spectra obtained with a CO₂ laser. The closest observed coincidence is *R*(53) *F*₁⁹ of ²⁸SiF₄, at -1.391 MHz from ¹²C¹⁶O₂ *P*(30). Implications for isotope-enrichment experiments are discussed.

The infrared-active stretching fundamental (ν_3) of silicon tetrafluoride is centered at 1031 cm⁻¹, overlapping the *P* branch of the 9.4- μm (00⁰1-02⁰0) band of the CO₂ laser. Several experiments involving pumping of ν_3 of SiF₄ with 9.4- μm CO₂ laser radiation have been reported, including saturation spectroscopy,¹⁻⁵ the observation of photon echoes,⁶ laser-induced fluorescence and dissociation,⁷⁻⁹ silicon isotope separation,¹⁰ and the use of vibrationally excited SiF₄ as an inert sensitizer for inducing chemical reactions.^{11,12} A full understanding of these effects depends on the identification of the SiF₄ absorptions that are in resonance with the various CO₂ laser frequencies. We report here the assignment of all ²⁸SiF₄ transitions from the vibrational ground state that fall near the ¹²C¹⁶O₂, ¹³C¹⁶O₂, ¹²C¹⁸O₂, and ¹³C¹⁸O₂ lines from 1023 to 1038 cm⁻¹. These assignments will be useful in the design and interpretation of infrared-microwave and infrared-radio-frequency double-resonance experiments. This work is the first

step in a systematic study of the $n\nu_3$ vibrational ladder of SiF₄, which we are undertaking to elucidate the

Table 1. ν_3 Spectroscopic Constants of ²⁸SiF₄ ^a

	Diode Data	Saturation Data
Scalar constants		
<i>m</i>	1031.39661(13)	1031.39700(14)
<i>n</i>	0.127726(4)	0.127727(4)
<i>p</i> × 10 ⁴	-2.5489(20)	-2.5559(20)
<i>v</i> × 10 ⁴	-3.7872(27)	-3.7892(23)
<i>q</i> × 10 ⁸	-1.36(18)	-1.84(18)
<i>s</i> × 10 ⁹	-1.10(6)	-0.85(6)
<i>w</i> × 10 ¹⁰	2.0(11)	[0] ^b
Tensor constants		
<i>g</i> × 10 ⁵	4.1171(23)	4.180(6)
<i>h</i> × 10 ⁸	3.15(5)	3.12(6)
<i>k</i> × 10 ¹⁰	1.28(13)	1.10(30)
<i>u</i>	[0] ^b	[0] ^b
Goodness of fit		
<i>N</i>	216	51
σ	18 MHz	7.7 MHz

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

^b Indeterminate; fixed at zero.

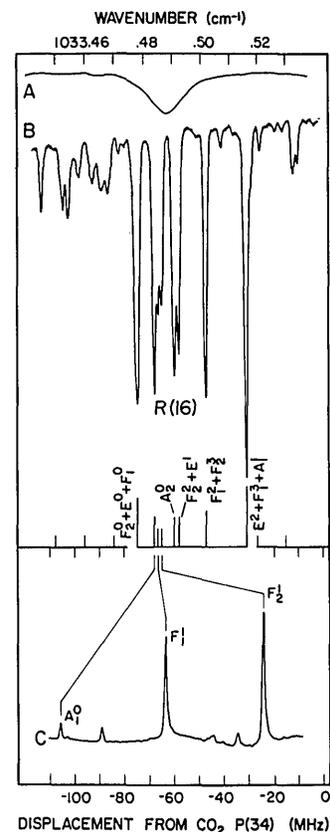


Fig. 1. Spectra of SiF₄ near the ¹²C¹⁶O₂ *P*(34) line. Trace A, taken with a tunable-diode laser, is the absorption that is due to 6.7-kPa (50-Torr) CO₂ in a 75-cm cell, showing *P*(34) at 1033.487999 cm⁻¹. Trace B, recorded simultaneously with A, is of 7-Pa (50-mTorr) SiF₄ in a 1.25-m cell at 198 K and displays the *R*(16) manifold. The transitions immediately to the low-frequency side of CO₂ *P*(34) are shown in detail in Trace C, a saturation spectrum of 4-Pa (30-mTorr) SiF₄. Line *A*₁⁰ appears weak because it is near the tuning limit of the CO₂ waveguide laser.

Table 2. SiF₄ Transitions within ±200 MHz of CO₂ Laser Lines

CO ₂ Line			ν(SiF ₄) - ν(CO ₂) (MHz)			CO ₂ Line			ν(SiF ₄) - ν(CO ₂) (MHz)				
I ^a	Ident.	ν	28SiF ₄ Transition	Observed			I ^a	Ident.	ν	28SiF ₄ Transition	Observed		
				Calc.	Satn.	Diode ^b					Calc.	Satn.	Diode ^b
838	R(16)	1037.8840	R(54) F ₂ (12)+F ₁ (12)	+162	636	R(18)	continued	Q(28) F ₁ (2)	+118	+118.629	} +95
			R(55) E(1)+F ₁ (2)+A ₁ (0)	+42	+41.030	...				Q(29) A ₂ (1)	+103	+101.968	
828	P(56)	1037.6096	R(52) E(7)+F ₂ (11)+A ₂ (3)	+130				Q(27) F ₂ (3)	+35	+34.495	} +25
			R(55) F ₂ (10)	-193				Q(21) F ₂ (0)+F ₁ (0)	-31	-32.188	
626	P(30)	1037.4341	R(53) F ₂ (8)	+187	...	+205				Q(27) F ₁ (3)	-33	} -33.401	} -30
			E(5)	+114	+124.314	+130				Q(29) F ₂ (4)	-33		
			F ₁ (9)	-15	-1.391 ^c	-5				Q(28) F ₂ (3)	-80	-81.047	...
636	R(28)	1037.1671	R(50) F ₂ (5)	+143				Q(31) A ₂ (2)	-132	-129.369	...
			F ₁ (5)	+83	+87.029	...				Q(26) F ₁ (3)	-147	-147.829	...
			R(47) F ₂ (0)+F ₁ (0)	+87	+78.378	...				Q(29) F ₁ (5)	-164	...	} -180
			R(49) E(2)+F ₁ (4)+A ₁ (1)	-55	-56.759	...				Q(31) F ₂ (6)	-169	...	
838	R(14)	1036.6725	R(45) F ₁ (6)	+65	+65.069	...				Q(26) F ₂ (4)	-170
			F ₂ (6)	-10	-12.254	...				Q(23) E(0)+F ₂ (1)+A ₂ (0)	-178
			R(46) F ₁ (0)+E(0)+F ₂ (0)	-21	-42.175	...	838	R(4)	1030.2953 ^d	Q(42) A ₂ (3)+F ₂ (10)+E(6)	+131
636	R(26)	1036.0170	R(37) F ₁ (0)+F ₂ (0)	+158				Q(44) F ₁ (9)+F ₂ (10)	+21
828	P(58)	1035.6992	R(36) F ₁ (1)	+7	636	R(16)	1029.8351 ^d	P(12) F ₂ (2)	-129	-144.226	...
			E(0)	-2				F ₁ (1)	-158
			F ₂ (1)	-10	626	P(38)	1029.4421 ^d	P(15) F ₁ (0)	+179	...	} +190
			R(34) F ₁ (0)	-139	-147.223	...				F ₂ (0)	+178	...	
			E(0)	-140	-147.989	...	838	R(2)	1028.9558	(none)
			F ₂ (0)	-140	-148.742	...	636	R(14)	1028.5119	(none)
838	R(12)	1035.4398	R(33) F ₁ (3)	+68	+68.162	...	838	R(0)	1027.5950	P(28) F ₁ (2)	+117
			F ₂ (3)	+60	+60.810	...				E(1)	-53
			R(32) A ₁ (2)+F ₁ (7)+E(5)	-76	-72.339	-55				F ₂ (2)	-98
636	R(24)	1034.8383	R(27) F ₁ (0)+F ₂ (0)	+198	626	P(40)	1027.3822	P(30) A ₁ (2)	-82	-96.155	} -110
838	R(10)	1034.1857	R(22) E(1)	+34	+39.038	...				F ₁ (5)	-83	} -96.550	
			F ₂ (2)	+6	+10.845	...				E(3)	-83		
			A ₂ (0)	-120	-116.265	...	636	R(12)	1027.1597	P(31) F ₁ (4)	+190
			F ₂ (1)	-190				F ₂ (5)	+16	+8.685	...
828	P(60)	1033.7717	(none)				E(3)	-118	-124.426	...
636	R(22)	1033.6308	(none)				F ₁ (5)	-164
626	P(34)	1033.4880	R(16) E(1)	+155	+160.376	} +150	636	R(10)	1025.7783	P(40) A ₂ (0)	+64	+70.977	...
			F ₂ (2)	+141	+145.993		...				F ₂ (1)	+58	+64.552
			A ₂ (0)	+99	+104.380	+90				F ₁ (1)	+52	+58.338	...
			F ₂ (1)	-30	-24.311	-30				A ₁ (0)	+46	+52.357	...
			F ₁ (1)	-69	-63.481	-75				P(41) F ₁ (3)	-88	-82.568	...
			A ₁ (0)	-111	-105.891	-120				F ₂ (3)	-88	-83.069	...
838	R(8)	1032.9102	(none)	838	P(2)	1025.5138	P(42) F ₁ (3)	+173
636	R(20)	1032.3945	R(7) F ₂ (1)	+196				A ₁ (1)	+85
			E(0)	+178	626	P(42)	1025.2979	(none)
			F ₁ (1)	+151	636	R(8)	1024.3677	P(50) F ₂ (7)	+42	+53.353	} +40
838	R(6)	1031.6134	(none)				F ₁ (6)	+36	+46.745	
626	P(36)	1031.4774	(none)				P(49) A ₁ (3)	-106	-105.771	} -110
636	R(18)	1031.1293	Q(33) A ₂ (2)	+206				F ₁ (11)	-108	-107.188	
			F ₂ (7)	+204				F ₂ (10)	-109	-108.591	
			F ₁ (8)	+201				A ₂ (3)	-111	-110.004	
			A ₁ (2)	+199	838	P(4)	1024.0996	P(52) E(5)+F ₂ (8)+A ₂ (2)	+185	...	+175
							626	P(44)	1023.1894	P(57) F ₁ (9)	-52	-75.421	-110

^a The isotopic species ¹²C¹⁶O₂, ¹³C¹⁶O₂, ¹²C¹⁸O₂, and ¹³C¹⁸O₂ are identified as 626, 636, 828, and 838, respectively.

^b Rounded to nearest 5 MHz.

^c Reported at (-1.5 ± 0.5) MHz by Beterov et al.³

^d There are also high-J (J > 50) Q-branch lines in this region.

general features of multiphoton absorption in this molecule.

The ν₃ band of SiF₄ was recorded by using a Ph_{1-x}Sn_xTe tunable semiconductor-diode laser source in a double-beam arrangement.¹³ The sample was cooled to 170–200 K to suppress hot-band structure. A total of 216 lines between 1023 and 1038 cm⁻¹ was measured, covering all or portions of most manifolds in the ranges P(13–59), Q(20–53), and R(5–56); all these lines were within ±0.1 cm⁻¹ of a CO₂ or OCS calibration feature.¹⁴

The usual formulas for the transition frequencies in the diagonal approximation are

$$\nu_{P,R}(M) = m + nM + pM^2 + qM^3 + sM^4 + \dots + (g - hM + kM^2 + \dots)\bar{F}(4),$$

$$\nu_Q(J) = m + vJ(J+1) + wJ^2(J+1)^2 + \dots + [-2g + uJ(J+1) + \dots]\bar{F}(4), \quad (1)$$

where $M = -J, (J+1)$ for P, (R)-branch transitions and the $\bar{F}(4)$'s are functions of tetrahedrally adapted fourth-rank tensor operators. Off-diagonal terms were included as corrections that were determined from a full diagonalization of the Hamiltonian. A fit of these equations to the diode data yielded the spectroscopic constants given in Table 1, and with this analysis we could identify transitions observed in Doppler-free saturated absorption using a CO₂ laser.

Both waveguide and free-space CO₂ lasers were used for the saturation spectroscopy. Their frequencies were shifted by acousto-optic modulators up to ±120 MHz in 40-MHz steps to obtain overlaps with the SiF₄ absorption lines.¹⁵ The spectroscopic laser was frequency referenced, by means of a voltage-swept rf oscillator, to a CO₂ laser that was stabilized to the standing-wave saturation resonance in a low-pressure (5.3-Pa) intracavity CO₂ absorption cell.¹⁶ A typical saturation spectrum is shown in Fig. 1. The output power was not

leveled and therefore varies across the scan, following the gain profile of the laser. Maximum intensity is near the center of the laser line (0-MHz displacement unshifted; $\pm n40$ MHz shifted), but absorption intensities cannot be normalized in a simple way because of the saturation phenomenon. The frequency of each saturated SiF₄ line was measured by adjusting the spectroscopic laser frequency (by means of the rf oscillator) to a point corresponding to the maximum absorption intensity and then measuring the offset rf. Measured frequencies of assigned saturated resonances near the ¹²C¹⁶O₂, ¹³C¹⁶O₂, and ¹³C¹⁸O₂ laser lines are given in Table 2.

The constants obtained by fitting Eqs. (1) to only the 42 saturation lines are also given in Table 1 and are in satisfactory agreement with those obtained from the diode data. The improvement in the second fit is limited by the fact that the Hamiltonian exhibits evidence of perturbations at high J : those 35 saturation frequencies for which $J < 42$ could be fitted with a standard deviation of 1.1 MHz. All transitions out of the vibrational ground state that are calculated to fall within ± 200 MHz of a laser line (using the second set of constants in Table 1) are summarized in Table 2; similar tabulations for other isotopic CO₂ lasers are available from the authors. The CO₂ frequencies used in this work are those of Petersen¹⁶ and Freed *et al.*¹⁷

The ¹²C¹⁶O₂ lines $P(30)$ to $P(34)$ pump the R branch of SiF₄, are inferred by Gutman and Heer⁶ from the polarization of photon echoes. The nearest coincidence is at CO₂ $P(30)$, which is offset by 1.4 MHz from $R(53)$ F_1^9 of ²⁸SiF₄; the latter transition has been proposed for frequency stabilization of the CO₂ laser.^{1,3} At CO₂ $P(32)$, Harter *et al.*⁴ illustrate the FEF triplet of $R(34)$ at -148 MHz; they also show an AFFA cluster at ~ -37 MHz that belongs to a hot band, which is as yet unassigned. (At 300 K, 30% of ²⁸SiF₄ molecules are in the ground vibrational state, 17% in $\nu_2 = 1$, 14% in $\nu_4 = 1$, 8% in $\nu_2 = \nu_4 = 1$, and 7% in $\nu_2 = 2$.)

¹²C¹⁶O₂ $P(36)$ falls between $Q(1)$ and $R(0)$ of ²⁸SiF₄, separated by 2.43 GHz from the former and 1.41 GHz from the latter. There are, however, several hot-band or isotopic absorptions in this region, including a strong line of -3.643 MHz from CO₂ $P(36)$ (reported at $+2.4$ MHz by Beterov *et al.*³). In the isotope-enrichment experiments of Lyman and Rockwood,¹⁰ SiF₄ was pumped with CO₂ $P(36)$ because the latter line appears to coincide with the SiF₄ Q branch as observed at low resolution.^{3,10} The present results, however, show that $P(36)$ does not pump any transition out of the vibrational ground state of ²⁸SiF₄. This may help to explain the results of Lyman and Rockwood, who found the laser-induced reaction of SiF₄ with H₂ to be inefficient, with poor isotopic selectivity.

The ¹²C¹⁶O₂ $P(J \geq 38)$ lines pump the P branch of ²⁸SiF₄. There are no near coincidences with ground-state transitions, but there are numerous hot-band absorptions that are close to the CO₂ laser lines.

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