

## Abstract

Doppler-limited tunable diode laser spectra of  $\nu_4$  of  $^{28}\text{SiF}_4$  have been analyzed and the spectroscopic constants determined. In contrast to most earlier low-resolution studies, the Coriolis constant  $\zeta_4$ , when combined with  $\zeta_3$  as obtained from previous laser spectroscopy, yields a zeta sum that is within 5% of the expected harmonic value of  $\frac{1}{2}$ . The band origins of 12 overtones and combinations have been obtained from Fourier-transform spectra (0.04  $\text{cm}^{-1}$  resolution), resulting in estimates of the anharmonicity constants and harmonic frequencies. From the Coriolis constants and the isotope shifts in  $\nu_3$  we have redetermined the general quadratic force field of  $\text{SiF}_4$ .

# Infrared spectrum and potential constants of silicon tetrafluoride<sup>a)</sup>

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## INTRODUCTION

Interest in the spectroscopy of  $\text{SiF}_4$  has been stimulated by the fact that its  $\nu_3$  fundamental at 1031  $\text{cm}^{-1}$  overlaps the *P* branch of the 9.4  $\mu\text{m}$  band of the  $\text{CO}_2$  laser. Pumping  $\text{SiF}_4$  with laser radiation has led to numerous studies of saturation spectroscopy,<sup>1-6</sup> photon echoes,<sup>7,8</sup> and laser-induced multiphoton excitation resulting in luminescence,<sup>9-14</sup> dissociation,<sup>9,10,12,13,15</sup> silicon isotope separation,<sup>16</sup> and intermolecular energy transfer.<sup>17-19</sup> Recently, the  $\nu_3$  band has been analyzed using both Doppler-limited diode laser spectroscopy<sup>20</sup> and sub-Doppler saturation spectroscopy,<sup>6</sup> and the transitions that are in near resonance with  $\text{CO}_2$  laser lines have been identified.<sup>6</sup> In addition, the  $3\nu_3$  band has been analyzed and the anharmonicity constants governing the  $n\nu_3$  vibrational ladder determined.<sup>21</sup> We now report a study of the other infrared-active absorptions and a redetermination of the general quadratic force field.

The force constants of  $\text{SiF}_4$ , established using Coriolis constants and isotopic frequency shifts as the necessary additional constraints to fix the three constants in the  $2 \times 2 F_2$  symmetry block, have been reported in at least nine different investigations.<sup>22-30</sup> Unfortunately, these force fields have not been in good agreement; the reported value of the off-diagonal symmetry force constant  $F_{34}$ , for example, has varied from 0.04 to 0.38  $\text{mdyn}/\text{\AA}$ .<sup>31</sup> The problem appears to lie in the determination of the Coriolis constants  $\zeta_3$  and  $\zeta_4$  from the unresolved contours of the corresponding fundamentals. The stretching mode  $\nu_3$  is not well suited for the determination of  $\zeta_3$  because of hot-band interference overlapping the *P* branch. While  $\nu_4$  seems to have an ideal contour for this purpose, the  $\zeta_4$ 's actually obtained from these measurements have not yielded force constants that agree with those provided by isotopic frequency shifts. In addition, all of these papers used observed rather than harmonic frequencies for the fundamentals.

With modern high-resolution techniques the vibration-rotation bands of heavy spherical-top molecules can be resolved and accurate values of the Coriolis constants

obtained, thus removing the uncertainty that is inevitable when these must be estimated from unresolved band contours. We will show that  $\zeta_3$  and  $\zeta_4$  are consistent with each other and with the frequency shifts, and that these parameters yield a force field determined to within relatively small limits. In addition, we have examined the spectra of the overtone and combination bands in order to estimate the anharmonicity constants and the harmonic fundamental frequencies.

## EXPERIMENTAL DETAILS

$\text{SiF}_4$  was obtained from Matheson Gas Products, and was further purified by trap-to-trap fractionation to reduce the amounts of air,  $\text{SO}_2$ ,  $\text{CO}_2$ , and  $\text{Si}_2\text{OF}_6$ , which were the principal impurities.

Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet Instruments Model 7199 FTIR spectrometer using 100 interferograms per run, and with an unapodized instrumental resolution of 0.04  $\text{cm}^{-1}$ . The sample was contained in a folded-path White cell, with pressure-path products of 1.1 to  $10^5$  Torr cm; pressures were measured with a capacitance gauge accurate to  $\pm 0.2\%$ . On this instrument, the calibration correction has been found to be proportional to wave number, and it was established in the 4.3  $\mu\text{m}$  region with absorption lines arising from the small amount of residual  $\text{CO}_2$  present in the sample.<sup>32</sup>

Doppler-limited spectra of  $\nu_4$  were obtained using a  $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$  tunable semiconductor diode laser from Laser Analytics Division of Spectra-Physics Inc. This was mounted in a standard configuration<sup>33</sup> using a Cu-doped germanium detector operating at liquid helium temperature. Sample cell lengths were 10 cm ( $p = 5$  to 11 Torr) and 16 cm ( $p = 0.3$  to 1.5 Torr). The scan rate was calibrated using an air-spaced etalon having a free spectral range of 0.02999  $\text{cm}^{-1}$ . Absolute wave number markers were provided by the spectrum of  $\text{CS}_2$ ,<sup>34</sup> and every measured line was within 0.15  $\text{cm}^{-1}$  of a calibration frequency. Although sample, etalon, and  $\text{CS}_2$  spectra were not recorded simultaneously, the rms error in the calibration lines, as measured from a single strong  $\text{CS}_2$  transition, was 0.002  $\text{cm}^{-1}$  or better over scan ranges of  $\sim 0.6$   $\text{cm}^{-1}$ . Repeated runs indicated

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that the reproducibility of measured SiF<sub>4</sub> frequencies (scan range < 0.15 cm<sup>-1</sup>) was of the order of 0.0010 cm<sup>-1</sup>.

### THE FUNDAMENTALS $\nu_3$ AND $\nu_4$

The usual formulas for the rovibrational transition wave numbers in a spherical-top fundamental are, in the diagonal approximation,<sup>35,36</sup>

$$\nu_{P,R}(M) \approx m + nM + pM^2 + qM^3 + \dots + (g - hM + kM^2 + \dots) \bar{F}(4), \quad (1)$$

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

where  $M = -J$  and  $J+1$  for the  $P$  and  $R$  branches, respectively (with  $J$  referring to the ground state), and the  $\bar{F}(4)$ 's are eigenfunctions of tetrahedrally adapted fourth-rank tensor operators. Not explicit in Eq. (1) are contributions that are off diagonal in the rotational angular momentum  $R$ ; these are comparable in magnitude to the  $q$  and  $h$  terms. From initial values of the constants, off-diagonal corrections are calculated by diagonalization of Hecht's Hamiltonian,<sup>37</sup> and this process is iterated to convergence.

The analysis of  $\nu_4$  started from the FTIR spectrum, which exhibited an asymmetric  $Q$  branch with a sharp low-frequency edge at  $388.45 \pm 0.02$  cm<sup>-1</sup>. The manifold spacing was about 0.29 cm<sup>-1</sup>, and from this information and the details of the splitting patterns, individual manifolds could be assigned in the diode spectra of the  $P$  and  $R$  branches. A total of 126 transitions belonging to  $P(4, 5, 14, 19-21, 29, 32)$  and  $R(16, 17, 32, 37, 38, 50-53)$  and extending from 379.3 to 404.5 cm<sup>-1</sup> was used in the final least-squares fit.

The  $Q$  branch of  $\nu_4$  belongs to the "very asymmetric" class<sup>38</sup> ( $v/g < -4$ ) with a dense and overlapping rotational structure. It was analyzed by first synthesizing its contour for a range of values of  $v/g$ , using an empirically determined linewidth of  $5.55 \times 10^{-4}$  cm<sup>-1</sup> (FWHM; 118% of the Doppler width), until a match was obtained that was adequate for assignments to be made. The number of transitions in this branch that were suitable for the least-squares data base was limited due to extensive overlap and blending; some 73 were finally selected belonging to  $Q(3, 5, 7, 9, 10, 12-29, 31, 32, 34, 36)$ . The final standard deviation of the fit, using all 199 frequencies, was 0.00085 cm<sup>-1</sup>, and the resulting constants are given in Table I. This table also lists for comparison the corresponding constants of  $\nu_3$  as determined previously.<sup>6</sup> Since the  $\nu_3$  data were more precise, additional constants besides those of Eq. (1) and Table I were determined for this band; see the original papers for details.<sup>6,20</sup>

Although both the  $\nu_3$  and  $\nu_4$  bands were analyzed satisfactorily in the manner described, we note that the presently derived value of  $(B\zeta)_4 = -0.00751$  cm<sup>-1</sup> is quite small. Because Eq. (1) is based on perturbation theory<sup>35</sup> with an energy denominator that is proportional to  $(B\zeta)J$ , the perturbation series converges more slowly than usual, especially as  $J$  increases.<sup>39</sup> Thus, for  $J$  greater than about 20, it was necessary to perform the full diagonalization since the diagonal approximation was inadequate. Properties of energy levels of a funda-

TABLE I. Analyses of  $\nu_3$  and  $\nu_4$  of <sup>28</sup>SiF<sub>4</sub>.<sup>a</sup>

	$\nu_3^b$	$\nu_4$
Spectroscopic constants		
$m$	1031.396 8(3)	388.444 82(14)
$n = B' + B_0 - 2(B\zeta) + 10\delta$	0.127 727(3)	0.288 677(6)
$[p = B' - B_0 + 4\delta] \times 10^4$	-2.552(5)	1.513 0(24)
$[v = B' - B_0 - 8\delta] \times 10^4$	-3.787 8(18)	2.023(3)
$[q \approx -4D] \times 10^7$	-0.16(3)	-2.40(5)
$g \times 10^5$	4.177 5(21)	-1.997(8)
$h \times 10^8$	3.14(4)	-7.1(3)
$k \times 10^{10}$	1.25(12)	4.5(7)
Molecular constants		
$[B' - B_0 = Y] \times 10^4$	-2.965(11)	1.682 9(22)
$B'^c$	0.136 46(3)	0.136 93(3)
$[Z_s = -12\delta = v - p] \times 10^4$	-1.236(5)	0.510(3)
$B\zeta$	0.072 80(2)	-0.007 51(2)
$\zeta$	0.533 5(8)	-0.054 9(6)

<sup>a</sup>All constants in cm<sup>-1</sup> except  $\zeta$ , which is dimensionless;  $1\sigma$  errors, in units of the last figure quoted, are given in parentheses.

<sup>b</sup>Weighted mean of diode and saturation results (Ref. 6).

<sup>c</sup>Using  $B_0 = 0.136 76(3)$  cm<sup>-1</sup>.

mental state with  $(B\zeta) \approx 0$  have been discussed in Ref. 40.

Calculation of the Coriolis constants  $\zeta_i$  proceeds as follows. From the analysis of  $3\nu_3$ , Patterson and Pine<sup>21</sup> report

$$B_0 = 0.136 76(3) \text{ cm}^{-1}.$$

This value of  $B_0$  corresponds to  $r_0 = 1.559 82(17)$  Å, which compares with average bond lengths determined by electron diffraction of (quoting  $1\sigma$  errors) 1.54(2),<sup>41</sup> 1.55,<sup>42</sup> 1.552(1),<sup>43</sup> and 1.555(2)<sup>44</sup> Å, and with 1.56(1) Å reported for the solid by x-ray diffraction.<sup>45</sup> For each band we can now calculate  $B'$  and  $\delta$ , and, from the spectroscopic constant  $n$ , the values of  $B\zeta$  given in Table I. The Coriolis constants are then obtained from  $\zeta_i = (B\zeta)_i / B'$ . This is actually an approximation that ignores the contribution of certain higher order scalar vibration-rotation perturbation constants<sup>37</sup> whose values are unknown, although they are expected to be small. Because of this uncertainty, the errors given for the  $\zeta_i$  in Table I are actually four times those obtained by simple propagation of the errors in  $B\zeta$  and  $B'$ .

The zeta sum is 0.478 6(10), within 4.3% of the expected harmonic value of 1/2. While this resolves some of the previous discrepancies between the two Coriolis constants, we might have expected closer agreement with the sum rule, considering that these observed  $\zeta$ 's are based on detailed band analyses. The difference may result from a Coriolis perturbation of  $\nu_3$ , discussed further below. We note that for SF<sub>6</sub>,  $\zeta_3 + \zeta_4 = 0.4771$ ,<sup>46</sup> similar to the value obtained here for SiF<sub>4</sub>.

Despite the apparent problems with the unresolved contour of  $\nu_3$ , several previous investigators<sup>26,27,29,30</sup> derived essentially correct values of  $\zeta_3$  (one exception is  $\zeta_3 = 0.63$  as obtained from the Raman spectrum<sup>28</sup>). On the other hand, the previously reported values of  $\zeta_4$  range from -0.07 to -0.12. We have remeasured the  $P$ - $R$  branch spacing of  $\nu_4$  with a carefully calibrated grating spectrometer, and we obtain  $\Delta\nu_{PR} = 23.82(20)$

TABLE II. Band origins of principal absorptions in <sup>28</sup>SiF<sub>4</sub>.

Band	$W$	$W_r$	$m_{\text{obs}}$ (cm <sup>-1</sup> )	Method <sup>a</sup>	$m_{\text{calc}}$ (cm <sup>-1</sup> )	Intensity <sup>b</sup>
$\nu_2$	$G_{22}$	0	264.2(10) <sup>c</sup>	...	264.2	(R)
$\nu_4$	$2G_{44}$	$-2B\zeta_4$	388.4448(2)	A	388.4	500
$2\nu_4$ ( $l_4=2$ )	$6G_{44}-8T_{44}$	$+2B\zeta_4$	776.3(5)	Ql?	776.3	0.9
$\nu_1$	0	0	800.6(3) <sup>d</sup>	...	800.6	(R)
$\nu_3$	$2G_{33}$	$-2B\zeta_3$	1031.3968(3)	A	1031.397	5000
$\nu_1+\nu_2$	$G_{22}$	0	1064.2(4)	Qs?	1064.2	1.1
$3\nu_4$ ( $l_4=1$ )	$7G_{44}+6T_{44}-[(5G_{44}+6T_{44})^2+384T_{44}^2]^{1/2}$	$-2B\zeta_4$	1164.2(2)	Ql	1164.1	1.4
$\nu_1+\nu_4$	$2G_{44}$	$-2B\zeta_4$	1189.7(3)	A	1189.7	40
$\nu_2+\nu_3$	$G_{22}+2G_{33}+8T_{23}$	$-2B\zeta_3$	1294.05(10)	Qh	1294.1	2.4
$\nu_3+\nu_4$ ( $l=2$ )	$2(G_{33}+G_{44})+G_{34}+(2/3)S_{34}-4T_{34}$		1418.75(10)	Qh	~1419	0.1
$\nu_3+2\nu_4$	e		1804.5(1)	Qh	~1804	0.7
$\nu_1+\nu_3$	$2G_{33}$	$-2B\zeta_3$	1828.17(2)	Qh	1828.2	7
$2\nu_3$ ( $l_3=2$ )	$6G_{33}-8T_{33}$	$+2B\zeta_3$	2059.1(3)	Qh	2059.105	1.2
$\nu_1+\nu_3+2\nu_4$	e		2602.55(10)	Qh	~2602	0.007
$2\nu_1+\nu_3$	$2G_{33}$	$-2B\zeta_3$	2623.8(1)	Qh	2623.9	0.015
$3\nu_3$ ( $l_3=1$ )	$7G_{33}+6T_{33}-[(5G_{33}+6T_{33})^2+384T_{33}^2]^{1/2}$	$-2B\zeta_3$	3068.5(1)	Qh	3068.515	0.015

<sup>a</sup>Method of determining band origin: A = analysis of rotational structure; Qh (Ql) = position of high(low)-frequency edge of Q branch, corrected for effects of resolution and linewidth; Qs = estimated from the peak of an apparently symmetric Q branch.

<sup>b</sup>Relative intensity =  $10^4 \log_{10}(I_0/I)/l$  (cm)  $\times p$  (Torr), where  $I$  is measured at the position of maximum absorption as recorded at 300 K with 0.04 cm<sup>-1</sup> resolution. These figures are intended for comparison of relative strengths, and are only approximately accurate. (R) = Raman active only.

<sup>c</sup>Raman, Q branch maximum, Ref. 28.

<sup>d</sup>Calculated; see the text.

<sup>e</sup> $W$  is unknown; there are 3  $F_2$  levels, and it is uncertain which of these is responsible for the observed infrared band.

cm<sup>-1</sup> at  $T=303(2)$  K, or  $\zeta_4 = -0.104(10)$ , which is near the the weighted mean of all other determinations. The reason for the discrepancy from the true value of  $-0.055$  is not obvious, for the  $\nu_4$  band has well-defined  $P$  and  $R$  branches and would appear to be ideally suited to this type of measurement. We have noticed in the diode spectrum of  $\nu_4$  several series of strong hot-band transitions in the  $P$  and  $R$  branches. These presumably originate from the bending levels  $\nu_2$  and  $\nu_4$ ; at 300 K, the populations of the ground state and of  $\nu_2$ ,  $\nu_4$ ,  $\nu_2+\nu_4$ , and  $2\nu_2$  are 29.8%, 16.8%, 13.9%, 7.8%, and 7.1%, respectively. If the manifold spacings in these hot bands differ from that of  $\nu_4 \sim 0$ , the apparent  $P$ - $R$  branch separation observed for the composite band will be affected, and we suggest that this is what is happening. This emphasizes that Coriolis constants obtained from unresolved band contours must be used with caution; fortunately, the high resolution now available in the infrared makes reliance on such approximations unnecessary.

The isotope shifts in  $\nu_3$  have been redetermined by measuring the displacements of the sharp high-frequency edges of the  $\nu_3$  Q branches on expanded FTIR traces. We obtain 8.98(3) and 17.40(6) cm<sup>-1</sup> for the <sup>28</sup>SiF<sub>4</sub>-<sup>29</sup>SiF<sub>4</sub> and <sup>28</sup>SiF<sub>4</sub>-<sup>30</sup>SiF<sub>4</sub> shifts, respectively, which are in agreement with, but more precise than, those reported previously.<sup>22,27,30</sup> We attempted to remeasure the  $\nu_4$  shifts but were unsuccessful: the FTIR spectrum at 388 cm<sup>-1</sup> was too noisy because of operation near the limit of the beam splitter range, and the diode perversely refused to lase at the appropriate frequencies.

## OVERTONE AND COMBINATION BANDS

Infrared bands observed in this work are summarized in Table II. The assignments are straightforward and call for little comment, except possibly for  $\nu_1+\nu_2$ .

This symmetry-forbidden  $E$  combination appears by virtue of a Coriolis interaction with the strong nearby  $\nu_3$  fundamental. This assignment was first made by Heicklen and Knight,<sup>22</sup> who confirmed it by noting the absence of a <sup>28</sup>Si-<sup>30</sup>Si isotope shift. Apart from this, there is little evidence for perturbations in the infrared spectrum. In particular, there are no Fermi resonances involving the infrared-active fundamentals,<sup>24</sup> in contrast to CF<sub>4</sub>, where one must treat a  $\nu_3/2\nu_4$  resonance.<sup>47</sup> The Fermi resonance between  $\nu_1$  and  $2\nu_4$  in the Raman spectrum<sup>48</sup> is expected to be small and no correction was made for it.

The band origins in Table II were estimated as follows. Most of the overtones and combinations have very asymmetric Q branches with sharp edges on either the high- or low-frequency sides, indicating that all Q-branch transitions fall on one side of the band origin.<sup>35</sup> In these cases, the frequency at which the Q-branch absorption begins to rise above the background was measured, and the origin was determined by correcting this frequency for the effects of instrumental resolution (0.04 cm<sup>-1</sup>) and the estimated full width at half-maximum of a single transition, taken to be the convolution of the Doppler width and the pressure broadening. The latter was assumed to be 6 MHz/Torr, the value for CF<sub>4</sub> at 300 K.<sup>49</sup> When applied to  $\nu_3$  and  $\nu_4$ , this method yields band origins that are within 0.015 cm<sup>-1</sup> of those determined by full analyses of the rotational structure. A few of the bands have apparently symmetrical Q branches, and the origins of these are less accurately known.

Most of the overtone and combination bands exhibit rotational structure, but no attempt was made to assign and analyze these in the present work. In fact, because of the extensive hot-band structure, such analyses

would be much more straightforward using spectra obtained at reduced temperatures. Since  $\zeta_4$  has been the most elusive of the Coriolis constants, however, an analysis was carried out for  $\nu_1 + \nu_4$  to confirm its value. This included 27 lines from  $P(10)$  to  $P(32)$  and from  $R(13)$  to  $R(21)$ , and resulted in

$$m = 1189.7109(24) \text{ cm}^{-1},$$

$$n = 0.28719(7) \text{ cm}^{-1},$$

with a standard deviation of fit of  $0.006 \text{ cm}^{-1}$ . This assignment places the origin at what appears to be the proper place at the low-frequency edge of the Q branch, but hot-band lines interfere enough so that the possibility of a misassignment by one unit in  $J$  can not be ruled out. The value of  $m$  in Table II reflects this uncertainty. The constant  $n$  is relatively insensitive to the assignment; using  $n = 0.2872(3) \text{ cm}^{-1}$ , which represents a generous error estimate, and the approximation  $\zeta \approx 1 - (n/2B_0)$ , we obtain  $\zeta_4 = -0.05000(11)$ . This agrees well with the value determined from  $\nu_4$  itself.

### ANHARMONICITY CONSTANTS AND HARMONIC FREQUENCIES

The band origins  $m$  in Table II represent the vibrational energies referred to the ground vibrational state, and are given for a tetrahedral molecule to the second order of approximation by

$$m = \sum_i \omega_i v_i + \sum_i X_{i1} v_i (v_i + d_i) + (1/2) \sum_i \sum_{j \neq i} X_{ij} v_i (v_j + d_j) + W'(\text{quantum numbers; symmetry})$$

$$= \sum_i \omega_i^0 v_i + \sum_{i \neq j} X_{ij} v_i v_j + W'(\text{quantum numbers; symmetry}), \quad (2)$$

where

$$\omega_i^0 = \omega_i + X_{i1} d_i + (1/2) \sum_{j \neq i} X_{ij} d_j. \quad (3)$$

Here  $v_i$  is the vibrational quantum number of fundamental  $i$  (which has a harmonic frequency  $\omega_i$  and degeneracy  $d_i$ ) and  $\omega_i^0$  is the effective harmonic frequency.<sup>50</sup> The first two terms on the right-hand side of Eq. (2) give the unsplit manifold origin<sup>51</sup> of a vibrational transition. In the following, the manifold origin will be indicated by parentheses, and the position of the observed band origin will be designated  $m$ . For example,

$$m(2\nu_1 + \nu_3) = (2\nu_1 + \nu_3) + W',$$

where  $W'$  gives all second-order shifts of a vibrational level and splittings into its tetrahedral sublevels.

In many bands  $W'$  separates into two terms

$$W' = W + W_r, \quad (4)$$

where the larger term  $W$  is associated with pure vibration<sup>37</sup> and  $W_r$  arises from the shift due to the  $J \cdot l$  term in the Hamiltonian. The energies  $W$  for the lower vibrational levels are given explicitly by Hecht,<sup>37</sup> and are listed for the bands of interest in Table II. In the overtones of  $F_2$  fundamentals a sufficient condition for the separability in Eq. (4) is that

$$|G_{ii}| \gg |T_{ii}| \gg |2B\xi_i J|, \quad (5)$$

a requirement that is met for  $i=3$  in the observed SiF<sub>4</sub> spectra,<sup>21</sup> and for  $i=4$  in the model SiF<sub>4</sub> calculations of Heenan.<sup>52</sup> When Eq. (5) is satisfied, one can write

$$W_r = -2B\xi_{\text{eff}},$$

where, for example,  $\xi_{\text{eff}}(2\nu_i) = -\xi_i^{53}$  and  $\xi_{\text{eff}}(3\nu_3, l=1) = \xi_3$ .<sup>54</sup>

For the present purposes we require the four  $\omega_i$ 's. Each  $\omega_i$  is determined from Eq. (3) if  $\omega_i^0$  and the four  $X_{ij}$ 's can be obtained from overtones and combinations. (There is a total of ten  $X_{ij}$ 's.) However, it must be emphasized at the outset that because of the tetrahedral splittings, accurate  $X_{ij}$ 's require the various anharmonic constants that appear in  $W$ ; these in turn can be obtained only from detailed rovibrational analyses of the overtone and combination bands. Such a full treatment to determine any  $\omega_i$  for a heavy spherical-top molecule has yet to be carried out. Some of the necessary information is available, however, and for many of the remaining constants reasonable approximations can be made.

We begin by noting that band origins  $m$  are available for  $\nu_3$  and  $\nu_4$ , but not for the Raman-active fundamentals  $\nu_1$  and  $\nu_2$ . For  $\nu_1$ , this can be remedied as follows: from Eq. (2),

$$2X_{14} = m(\nu_1 + \nu_3 + 2\nu_4) - m(\nu_3 + 2\nu_4) + m(\nu_3) - m(\nu_1 + \nu_3),$$

yielding  $X_{14}$  as given in Table III. (This equation is valid because although  $W$  is unknown for  $\nu_3 + 2\nu_4$  and  $\nu_1 + \nu_3 + 2\nu_4$ , it is the same for the two bands, and similarly for  $W_r$ .) We can now obtain  $\nu_1$  from  $\nu_1 + \nu_4$ :

$$m(\nu_1) = (\nu_1) = m(\nu_1 + \nu_4) - m(\nu_4) - X_{14} = 800.6(3) \text{ cm}^{-1}.$$

This is in excellent agreement with  $\nu_1 = 800.8 \text{ cm}^{-1}$  as reported by Clark and Rippon<sup>28</sup>; their value represents a Q-branch maximum rather than a band origin, but for a totally symmetric fundamental the difference is expected to be small. Unfortunately, there is insufficient infrared data to similarly determine  $\nu_2$ , so we have used the Raman frequency,<sup>28</sup> assigning it an estimated uncertainty of  $\pm 1 \text{ cm}^{-1}$ . Model potential calculations by Heenan<sup>52</sup> indicate that  $G_{22} < 0.1 \text{ cm}^{-1}$ , so at this level of accuracy ( $\nu_2$ ) and  $m(\nu_2)$  can be considered identical.

The remaining  $X_{ij}$  involving  $\nu_1$  are then obtained straightforwardly:

$$2X_{11} = m(2\nu_1 + \nu_3) - 2m(\nu_1 + \nu_3) + m(\nu_3),$$

$$X_{1i} = m(\nu_1 + \nu_i) - m(\nu_1) - m(\nu_i), \quad (i=2, 3),$$

with the results given in Table III. Similarly,

$$X_{23} + 8T_{23} = m(\nu_2 + \nu_3) - m(\nu_2) - m(\nu_3).$$

Since  $T_{23}$  is of the order of  $10^{-2} \text{ cm}^{-1}$ ,<sup>52</sup> we can ignore its contribution within the uncertainty quoted for  $X_{23}$  in Table III. No bands involving  $X_{22}$  or  $X_{24}$  were observed in the present work, and these two constants were assumed to be zero. Heenan's calculations<sup>52</sup> suggest that they are both small ( $\ll 0.1 \text{ cm}^{-1}$ ).

For  $\nu_3$ , the vibrational ladder has been thoroughly characterized by Patterson and Pine<sup>21</sup> from an analysis

TABLE III. Vibrational parameters of <sup>28</sup>SiF<sub>4</sub>.<sup>a</sup>

	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3	<i>i</i> = 4
Γ <sub><i>i</i></sub>	A <sub>1</sub>	E	F <sub>2</sub>	F <sub>2</sub>
(ν <sub><i>i</i></sub> )	800.6(3)	264.2(10) <sup>b</sup>	1027.9768(12)	388.5(3)
ω <sub><i>i</i></sub> <sup>0</sup>	801.2(3)	264.2(11)	1030.9826(14)	388.7(3)
ω <sub><i>i</i></sub>	807.1(12)	267(3)	1044.2(12)	389.8(9)
X <sub><i>i1</i></sub>	-0.57(5)			
X <sub><i>i2</i></sub>	-0.6(11)	0.0(5)		
X <sub><i>i3</i></sub>	-3.8(3)	-1.5(10)	-3.0058(7) <sup>d</sup>	
X <sub><i>i4</i></sub>	+0.64(7)	0.0(5)	-0.5(4)	-0.22(10)
ξ <sub><i>i</i></sub>	(0)	(0)	0.5335(8)	-0.0549(6)
Δ <i>m</i> (ν <sub><i>i</i></sub> ) ( <sup>28</sup> Si- <sup>29</sup> Si)	...	...	8.98(3)	1.55(52) <sup>e</sup>
Δ <i>m</i> (ν <sub><i>i</i></sub> ) ( <sup>28</sup> Si- <sup>30</sup> Si)	...	...	17.40(6)	3.00(18) <sup>e</sup>
Δω <sub><i>i</i></sub> ( <sup>28</sup> Si- <sup>29</sup> Si)	(0)	(0)	9.33(9)	1.56(52)
Δω <sub><i>i</i></sub> ( <sup>28</sup> Si- <sup>30</sup> Si)	(0)	(0)	18.09(18)	3.01(18)

<sup>a</sup>All constants are in cm<sup>-1</sup> except ξ<sub>*i*</sub>, which is dimensionless; standard deviations, in units of the last figure quoted, are given in parentheses.

<sup>b</sup>Raman: Clark and Rippon (Ref. 28); the uncertainty (unstated) was assumed to be ±1 cm<sup>-1</sup>.

<sup>c</sup>The effective harmonic frequency ω<sub>*i*</sub><sup>0</sup> = (ν<sub>*i*</sub>) - X<sub>*ii*</sub>; see Eq. (2).

<sup>d</sup>Patterson and Pine (Ref. 21).

<sup>e</sup>Heicklen and Knight (Ref. 22).

of 3ν<sub>3</sub>; they give

$$X_{33} = -3.0058(7), G_{33} = 1.7828(6), T_{33} = 0.20992(10) \text{ cm}^{-1}.$$

Since

$$m(\nu_3) = (\nu_3) + 2G_{33} - 2B\xi_3,$$

we obtain the vibrational level (ν<sub>3</sub>) as given in Table III. These constants reproduce the observed band centers *m* of 2ν<sub>3</sub> and 3ν<sub>3</sub> quite satisfactorily (Table II).

We have insufficient data for an accurate evaluation of X<sub>34</sub>. Ignoring the (minor) rotational correction,

$$X_{34} + G_{34} + (2/3)S_{34} - 4T_{34} = m(\nu_3 + \nu_4) - m(\nu_3) - m(\nu_4) \\ = -1.1(1) \text{ cm}^{-1}.$$

The additional constants are unknown, but Heenan<sup>52</sup> indicates that X<sub>34</sub>, G<sub>34</sub>, and -4T<sub>34</sub> are all negative and of similar magnitude while S<sub>34</sub> < 0.1 cm<sup>-1</sup>. If these calculations are approximately correct, we estimate that X<sub>34</sub> = -0.5(4) cm<sup>-1</sup>, where the uncertainty has been chosen to span the range of probable values.

For the ν<sub>4</sub> ladder, we assume that T<sub>44</sub> = 0 (Heenan's<sup>52</sup> calculation indicates < 0.1 cm<sup>-1</sup>), and we can then solve the ν<sub>4</sub>, 2ν<sub>4</sub>, 3ν<sub>4</sub> system to obtain

$$(\nu_4) = 388.5(3), X_{44} = -0.22(10), G_{44} = -0.05(15) \text{ cm}^{-1}.$$

For 3ν<sub>4</sub>, this assumes that the observed transition is to I<sub>4</sub> = 1, in analogy with 3ν<sub>3</sub>. We note that the intensity of 3ν<sub>4</sub> compared with that of 2ν<sub>4</sub> suggests that the former band may be in resonance with ν<sub>1</sub> + ν<sub>4</sub>, which increases the uncertainty of these parameters.

The anharmonicity constants are listed in Table III, which also gives the harmonic frequencies ω<sub>*i*</sub>, calculated from Eq. (3).

Finally, we obtain the isotope shifts corrected for anharmonicity by using the common approximation

$$X_{ij}^* = (\nu_i^* \nu_j^* / \nu_i \nu_j) X_{ij}, \quad (6)$$

where the asterisk indicates the heavier isotope. The

validity of Eq. (6) is uncertain, and it is particularly suspect for X<sub>14</sub> because of the ν<sub>1</sub>/2ν<sub>4</sub> Fermi resonance, but without a full treatment of the overtone and combination bands of the isotopic species, we have no alternative but to make an assumption of this kind. Equation (2) then yields

$$\Delta\omega_3 = \Delta m(\nu_3) - 4X_{33}[1 - (\nu_3^*/\nu_3)^2] - (1/2) \sum_{j \neq 3} d_j X_{3j} \\ \times [1 - (\nu_j^* \nu_3^* / \nu_j \nu_3)] - 2\Delta G_{33} + 2B'\Delta\xi_3,$$

and similarly for Δω<sub>4</sub>. The quantities ΔG<sub>33</sub> and ΔG<sub>44</sub> were estimated to be -0.03G<sub>33</sub> and -0.13G<sub>44</sub> amu<sup>-1</sup>, respectively, from Heenan's calculations,<sup>52</sup> and Δξ<sub>3</sub> and Δξ<sub>4</sub> were taken as -0.011 and +0.011 amu<sup>-1</sup>, respectively, based on the force field calculation that follows. The resulting Δω's are given in Table III; because of the uncertainty in the approximation of Eq. (6) and in the ΔG corrections, the errors in Δω<sub>3</sub> quoted there are 3σ, instead of 1σ as elsewhere in this paper.

## FORCE FIELD

We have four isotope shifts and two Coriolis constants to constrain the off-diagonal force constant in the F<sub>2</sub> symmetry block. The determination of F<sub>34</sub> using these

TABLE IV. Determination of the off-diagonal force constant F<sub>34</sub>.

Constraining parameter <i>P</i>	F <sub>34</sub> (mdyn/Å)	Δ <i>P</i> <sup>a</sup>
Δω <sub>3</sub> ( <sup>28</sup> Si- <sup>29</sup> Si) = 9.33(9) cm <sup>-1</sup>	0.192(26)	+0.04 cm <sup>-1</sup>
Δω <sub>3</sub> ( <sup>28</sup> Si- <sup>30</sup> Si) = 18.09(18) cm <sup>-1</sup>	0.189(27)	+0.10 cm <sup>-1</sup>
Δω <sub>4</sub> ( <sup>28</sup> Si- <sup>29</sup> Si) = 1.56(52) cm <sup>-1</sup>	0.26(44)	+0.07 cm <sup>-1</sup>
Δω <sub>4</sub> ( <sup>28</sup> Si- <sup>30</sup> Si) = 3.01(18) cm <sup>-1</sup>	0.23(7)	+0.07 cm <sup>-1</sup>
ξ <sub>3</sub> = 0.5335(8)	0.2596(21)	-0.0214
ξ <sub>4</sub> = -0.0549(6)	0.2041(16)	0.0000
Weighted average <sup>b</sup>	0.204(2)	

<sup>a</sup>Δ*P* = observed value of the parameter minus the value calculated using the force field of Table V.

<sup>b</sup>Weighted according to the inverse square of the estimated errors; ξ<sub>3</sub> result not included.

TABLE V. Symmetry and valence force constants of SiF<sub>4</sub>.

	(mdyn/Å)
$F_{11} = f_r + 3f_{rr}$	7.292(22)
$F_{22} = f_\alpha - 2f_{\alpha\alpha} + f'_{\alpha\alpha}$	0.266(6)
$F_{33} = f_r - f_{rr}$	6.374(16)
$F_{44} = f_\alpha - f'_{\alpha\alpha}$	0.4447(22)
$F_{34} = \sqrt{2}(f_{r\alpha} - f'_{r\alpha})$	0.204(2)
$f_r$	6.603(13)
$f_{rr}$	0.230(7)
$f_\alpha - f_{\alpha\alpha}$	0.355(3)

constraints is summarized in Table IV.<sup>55</sup> The Coriolis constants determine the force constant most precisely, but these two results differ by many times their estimated uncertainties. This is, of course, a consequence of the fact that  $\zeta_3$  and  $\zeta_4$  do not exactly satisfy the sum rule. It is not immediately obvious which of the Coriolis constants is to be preferred, but the close agreement of  $F_{34}$  as obtained from  $\zeta_4$  and from the various isotope shifts (all of which yield  $F_{34} = 0.19$  to  $0.23$  mdyn/Å) leads us to prefer this value. Consequently, the  $\zeta_3$  determination of  $F_{34}$  was not used in obtaining a final value for this force constant. The value that we have selected is the weighted average of all results except that from  $\zeta_3$ , and is essentially that fixed by  $\zeta_4$ , which is much more precise than any of the isotope shifts.

We emphasize that while a Coriolis constant obtained from high-resolution spectroscopy may appear to fix a force field with high precision, this can be accepted as real only if both Coriolis constants can be determined and shown to obey the sum rule exactly. In the present case, we assume that  $\nu_3$  is perturbed in some way that affects  $\zeta_3$ : the Coriolis interaction between  $\nu_3$  and  $\nu_1 + \nu_2$ , which are separated by only  $33 \text{ cm}^{-1}$ , is known to be significant since it enables the symmetry-forbidden  $\nu_1 + \nu_2$  band to appear in absorption. On the other hand,  $\nu_4$  is some  $124 \text{ cm}^{-1}$  removed from any other transition, and  $\zeta_4$  is consequently less subject to the influence of perturbations.

The final symmetry force constants are listed in Table V. The errors quoted there reflect the uncertainties in the harmonic frequencies  $\omega_i$ , and, for  $F_{33}$  and  $F_{44}$ , the uncertainty in  $F_{34}$  as well. This table also gives the relations between the symmetry and valence force constants, and derived values of the latter.

Table VI gives the resulting eigenvector and potential

TABLE VI. Eigenvector and potential energy matrices.<sup>a</sup>

	$\omega_3 = 1044.2 \text{ cm}^{-1}$	$\omega_4 = 389.8 \text{ cm}^{-1}$
$L_3$	0.31618(3)	0.0180(5)
$L_4$	-0.3262(11)	0.4353(8)
$V_{33}$	0.992	0.023
$V_{44}$	0.074	0.941
$V_{34}$	-0.066	0.036

<sup>a</sup>Units for  $L$ -matrix elements:  $\text{amu}^{-1/2}$ .

TABLE VII. Vibrational amplitudes and shrinkage effects in SiF<sub>4</sub> (Å).

	Calculated		Observed ( $T = 298 \text{ K}$ )	
	$T = 0 \text{ K}$	$T = 300 \text{ K}$	Hagen and Hedberg <sup>a</sup>	Beagley <i>et al.</i> <sup>b</sup>
$u$ (Si-F)	0.03868	0.03908(1)	0.0434(9)	0.029(7)
$u$ (F...F)	0.0608	0.0719(3)	0.0743(17)	0.071(3)
$\delta$ (F...F)	0.00180	0.00244(1)	0.000(2)	0.006(4)

<sup>a</sup>Reference 43.

<sup>b</sup>Reference 44.

energy matrices for the  $F_2$  block. The errors quoted for the eigenvectors represent the propagation of the uncertainties in both the frequencies and force constants. From this  $L$  matrix the vibrational amplitudes and shrinkage effect were calculated; these are listed in Table VII and compared with the results of the two most recent electron diffraction experiments. The agreement is generally satisfactory.

The alternate force field for the  $F_2$  block is  $F_{33} = 1.680$ ,  $F_{44} = 2.792$ ,  $F_{34} = 1.377$  mdyn/Å. In addition to being unreasonable on physical grounds, this solution can be rejected at once on the basis of the Si-F amplitude it yields, which at 300 K is  $0.0658 \text{ Å}$  rather than the  $0.03$  to  $0.04 \text{ Å}$  indicated by the electron diffraction experiments (Table VII).

## DISCUSSION

The force field of Table V is appreciably better determined than any that has been reported heretofore. If it is assumed that the value of  $\zeta_3$  is perturbed, then  $\zeta_4$  and the isotope shifts are consistent in determining the force field. Because of uncertainties in correcting the observed isotope shifts in the band origins to harmonic values, however,  $\zeta_4$  fixes the force field much more accurately.

Further improvement can be expected only from detailed analyses of the spectra of <sup>29</sup>SiF<sub>4</sub> and <sup>30</sup>SiF<sub>4</sub>. These would clarify the isotopic dependence of the  $X_{ij}$  and of the tetrahedral splitting constants  $G_{22}$ ,  $G_{33}$ , and  $G_{44}$ , and would make possible a treatment of the  $\nu_3/(\nu_1 + \nu_2)$  and  $\nu_1/2\nu_4$  interactions.

Application of these results to potential modeling and to following the excitation and dissociation pathways of laser-pumped SiF<sub>4</sub> are in progress.

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