JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 72A, No. 3, May–June 1968

Force Field for SiF_4

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(January 29, 1968)

The force field of SiF_4 has been determined using both Coriolis coupling constants obtained from an investigation of the band contour of ν_3 at 195 °K and isotopic shifts. The force fields are equally well determined using both methods and are in agreement.

Key Words: Band contour, Coriolis constant, force field, infrared, isotopic shift, low temperature, SiF_4.

In determining the general valence force field for silicon tetrafluoride from various sources of molecular information, McKean [1][1] noted a significant discrepancy in the range of values for the stretch-bend interaction force constant characterized separately by the isotopic frequency shift $\Delta\nu_4$ and by the Coriolis constant ζ_4. Since the estimate of ζ_4 from the band shape of ν_4 contains a relatively large uncertainty, as a consequence of an inability to locate precisely the *P* and *R* branch maxima, we examine in this communication the contour of the ν_3 fundamental at 195 °K in order to obtain a reliable zeta value for constraining the force field. In addition to confirming the potential function for SiF_4 by comparing the force constants calculated from alternate methods, rotation-vibration interaction data from the two F_2 vibrations provide further tests concerning the utility of the band contour method for estimating Coriolis parameters.

The contours for both infrared active fundamentals, ν_3 and ν_4, were recorded at 310 and 195 °K with a double beam grating spectrophotometer equipped with interference filters to separate the orders. Spectral slit widths varied between 0.7 and 0.9 cm^{-1}. For low temperature measurements, a 5-cm path length copper cell, surrounded by an evacuated glass shell, was in contact with a solid CO_2 and acetone mixture.

Figure 1 displays a representative scan of the ν_3 contour at 310 and 195 °K. A hot band at approximately 1029 cm^{-1} distorts the contour sufficiently at 310 °K to preclude a valid *P–R* measurement for use in the Coriolis constant determination. The attenuation of the intensity of the hot band transition at 195 °K, however, reveals definite *P*, *Q*, and *R* branch features. Additional absorptions, attributed to the naturally occurring isotopes of ^{29}Si and ^{30}Si, are also observed. These values, summarized in table 1, agree well with Heicklen and Knight's frequencies obtained from isotopically enriched compounds [2].

For ν_3, an average value of 8.3 cm^{-1} for $\Delta\nu_{P\text{-}R}$ was determined from twelve expanded traces, recorded at several spectral slit widths. Repeated determinations of the *P* and *R* branch maxima by a second investigator suggests an uncertainty in $\Delta\nu_{P\text{-}R}$ of less than 0.5 cm^{-1}. For the ν_4 vibration, it is more difficult to determine $\Delta\nu_{P\text{-}R}$ owing to the relative broadness of the *P* and *R* branch features. Measurements in a 10-cm path length cell at 310 °K, with varying sample pressures and instrumental conditions, give 23.4 ± 1.0 cm^{-1} for

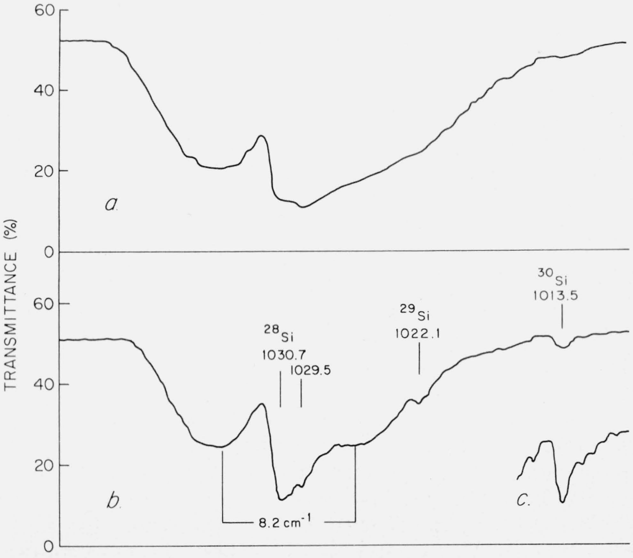

FIGURE 1. *The vibration-rotation band contour for the ν_3 fundamental of* SiF_4.

(a) 310 °K, (b) 195 °K, (c) 195 °K. The frequencies are labeled in cm^{-1}.

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[1] Figures in brackets indicate the literature references at the end of this paper.

$\Delta\nu_{P\text{-}R}$, in agreement with Heicklen and Knight's single value of 23.1 cm^{-1}.

TABLE 1. *Observed data for SiF$_4$*

$\Delta\nu_{P\text{-}R}$ represents the P–R separation in cm^{-1}. The frequencies are in cm^{-1}; the ζ_i are dimensionless.

Frequency (cm^{-1})	Assignment
1030.7	^{28}SiF$_4$
1029.5	hot band
1022.1	^{29}SiF$_4$
1013.5	^{30}SiF$_4$

	Observed frequency (cm^{-1})	$\Delta\nu_{P\text{-}R}$ (cm^{-1})	ζ_i	$\Sigma\zeta_i$	Sum rule
ν_3	1030.7	8.3 ± 0.5 [a, c]	0.53 ± 0.03		
ν_4	389.4	23.4 ± 1.0 [b]	-0.07 ± 0.05	0.46 ± 0.06	0.50

[a] 195 °K.

[b] 310 °K.

[c] The estimated uncertainty of 0.5 cm^{-1} represents twice the maximum deviation from the value obtained from averaging twelve traces of the spectrum.

Edgell and Moynihan's expression (3) in terms of the rotational constant B and absolute temperature T, relates the Coriolis constant ζ_i to the measured $\Delta\nu^i_{P-R}$ values. Perturbations to the contour from the ^{29}Si and ^{30}Si isotopes are ignored in this calculation. A summary of the calculated Coriolis constants appears in table 1. The zeta sum of 0.46 ± 0.06 for the two Coriolis values, compared to the theoretical sum of 0.50, supports the consistency of the data determined by the contour method.

The Coriolis coefficients ζ and the isotopic frequency shifts $\Delta\nu$, respectively, provide force field information through analogous expressions; namely

$$\zeta = L^{-1}C(L^{-1})', \tag{1}$$

and

$$\frac{2\Delta\nu}{\nu} = L^{-1}\Delta G(L^{-1})'. \tag{2}$$

L^{-1} represents the normal coordinate vector matrix; C is a function of the atomic masses and the molecular geometry, and ΔG represents the change in the G matrix as a result of isotopic substitution. Since the L matrix relates the force field to the experimental parameters, figure 2 presents plots of the dependence of ζ_i and $\Delta\nu_4$ upon the interaction force constant F_{34} for the F_2 symmetry species.

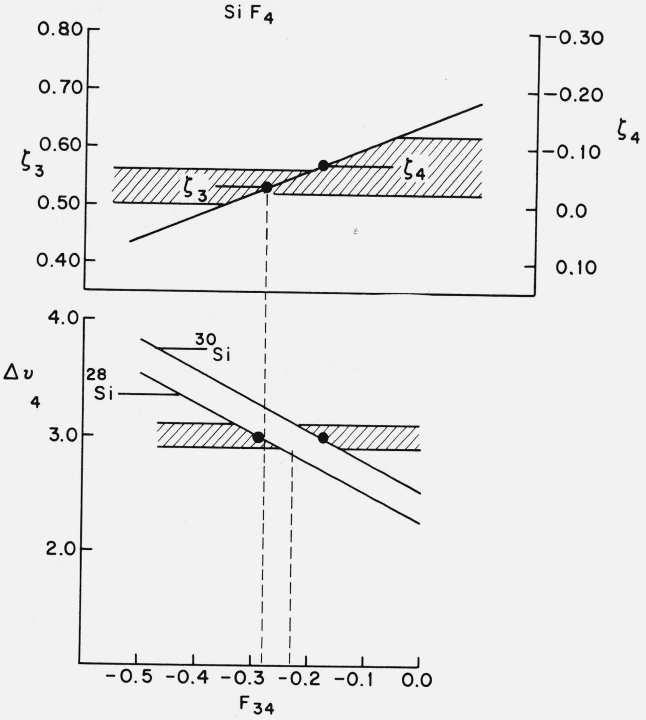

FIGURE 2. *Plots of ζ^z_{33}, ζ^z_{44},* and $\Delta\nu_4$ *(in cm^{-1}) as functions of* F_{34} *for the* F_2 *symmetry species of* SiF$_4$.

F_{34} is in millidynes per angstrom.

The use of eq (2) with the L^{-1} matrices for both the ^{28}S and ^{30}Si isotopes demonstrates the uncertainty in the force field fixed by a value for $\Delta\nu_4$. The lower portion of figure 2 displays the relevant plots. The solid circles locate the experimental point for $\Delta\nu_4$ of 3.0 ± 0.1 cm^{-1} (1, 2), while the shaded areas represent the uncertainty in the experimental measurement. A vertical dotted line gives the average value for F_{34} from the perturbation calculation. The solid circles and shaded areas in the upper portion of the figure represent the experimental Coriolis constants and their uncertainties, respectively. The vertical line originating from ζ_3 in the plot defines the preferred force field using the more certain Coriolis value. The L^{-1} matrix for the ^{28}Si species formed the basis for the Coriolis plot in the figure. Definitions for the symmetry coordinates, as well as the details of the vibrational calculation, appear in reference [4].

The force constants, constrained by (a) $\Delta\nu_4$, (b) ζ_3 and ζ_4, and (c) ζ_3 alone appear in table 2. The dispersions in the F's are assumed to arise from the uncertainties in the experimental data alone; that is, the errors due to anharmonicity and the uncertainty in

TABLE 2. SiF$_4$ *force constants constrained by* $\Delta\nu_4$, ζ_3 *and* ζ_4, *and* ζ_3, *respectively*

The units of F are expressed in millidynes per angstrom.

Force constant	$\Delta\nu_4$	ζ_3 and ζ_4	ζ_3
F_{33}	6.28 ± 0.22	6.21 ± 0.31	6.40 ± 0.16
F_{34}	-0.23 ± 0.10	-0.20 ± 0.15	-0.28 ± 0.07
F_{44}	$.44\pm0.01$	$.45\pm0.02$	$.44\pm0.01$

the normal coordinates are neglected. The very good agreement for the force fields between the two types of constraints confirms the potential function for SiF_4. Although the frequency shift method reflects an optimistic estimate of ± 0.1 cm^{-1} uncertainty in the $\Delta\nu_4$ measurement (1, 2), the estimated dispersions in the crucial interaction force constant F_{34} suggest that the Coriolis and the isotopic shift constraints are about equally effective for this molecule.

One of us (S.A.) acknowledges the support of the Air Force Office of Scientific Research, U.S. Department of Defense.

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(Paper 72A3–498)