# Molecular Constants of $GeCl_4$ and $SnCl_4$ from Coriolis Coupling Constants and an Appraisal of the Accuracy of the Method in Determining Force Fields, Mean Amplitudes and Shrinkage

R. Kebabçioglu, A. Müller, C. J. Peacock, and L. Lange

Anorganisch-Chemisches Institut der Universität Göttingen

(Z. Naturforsch. **23 a**, 703—708 [1968]; received 26 February 1968)

The Coriolis Coupling constants of $GeCl_4$ and $SnCl_4$ are obtained from the contours of the $\nu_4$ bands and used to determine the force fields. From consideration of these and that previously reported for $SiCl_4$ it is shown that even relatively inaccurate Coriolis constants can yield better force fields and Bastiansen-Morino shrinkage effects than experimental mean amplitudes of vibration; but that for $SnCl_4$, because of significant differences between usually valid approximate force fields and the Coriolis constant fixed one, a wrong value of the constant may have been obtained.

It is also shown that the force field obtained from Vol'kenshtein's theory of absolute Raman intensities is not very good for $GeCl_4$ and wildly inaccurate for $SnCl_4$.

By the method of Edgell and Moynihan [1] it is possible to calculate the Coriolis coupling constants $\zeta_3$ and $\zeta_4$ from the $\nu_3$ and $\nu_4$ band contours of tetrahedral $XY_4$ molecules. With these one may then completely define the force field for the $F_2$ species using the equations of Meal and Polo [2]. Whilst we have previously reported such a determination for $SiCl_4$ [3], the present work gives the Coriolis constants and force fields for $GeCl_4$ and $SnCl_4$, and presents a critical appraisal of the accuracy of the method for all three molecules, comparing it with force fields determined from mean amplitudes of vibration and from Raman absolute intensities (the Vol'kenshtein field [4]).

The band contours for the $\nu_4$ bands of $GeCl_4$ and $SnCl_4$ are shown in Figs. 1 and 2, neither $\nu_3$ band showing any structuring. From these the Coriolis

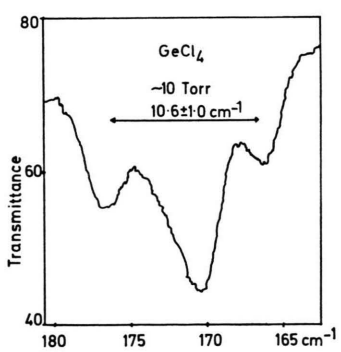


Fig. 1. $\nu_4$ band for $GeCl_4$.

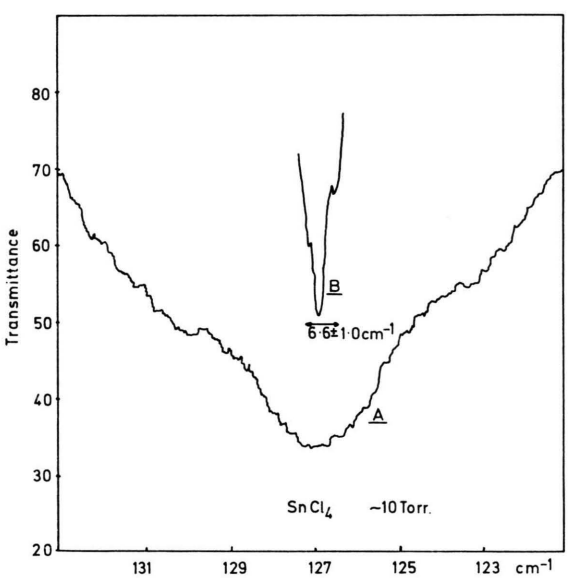


Fig. 2. $\nu_4$ band for $SnCl_4$. A is expansion of B.

constants were calculated from the separation of the P and R branches ($\Delta_{PR}\nu_4$) using the equation [1]:

$$\zeta_{44} = 1 - \tfrac{1}{4}(h\,c/B\,k\,T)^{1/2}\,\Delta_{PR}\,\nu_4$$

where $B$ is the rotational constant of the molecule and $T$ the absolute temperature.

The measured separations [4b], calculated constants, normal frequencies [4b] and other experimental molecular data are given in Table 1 for $GeCl_4$, $SnCl_4$ and,

[1] W. F. Edgell and R. E. Moyniham, J. Chem. Phys. **27**, 155 [1957].
[2] J. H. Meal and S. R. Polo, J. Chem. Phys. **24**, 1119, 1126 [1956].
[3] C. J. Peacock, A. Müller and R. Kebabcioglu, J. Mol. Spectr., in press.
[4] C. R. Vol'kenshtein, Acad. Sci. U.R.S.S. **32**, 185 [1941].

| | $SiCl_4$ [3] | $GeCl_4$ | $SnCl_4$ |
|---|---|---|---|
| $\Delta_{PR}\nu_4$ ($cm^{-1}$) | 15.0 ±0.3 $cm^{-1}$ | 10.6 ±1.0 $cm^{-1}$ | 6.6 ±1.1 $cm^{-1}$ |
| $\zeta_{44}$ | −0.221 ±0.027 | 0.10 ±0.08 | 0.38 ±0.11 |
| $r$ (Å) | 2.0193 ±0.0034 | 2.113 ±0.003 [12] | 2.31 ±0.08 |
| $\nu_1(A_1)$ ($cm^{-1}$) | 425 ±1 | 396 ±3 | 366 ±3 |
| $\nu_2$ (E) | 149 ±2 | 131 ±3 | 101.5 ±4 |
| $\nu_3$ ($F_2$) | 619.0 ±0.5 | 456 ±1 | 407 ±1 |
| $\nu_4$ ($F_2$) | 221.3 ±0.5 | 170.5 ±1 | 127.2 ±1 |
| $U_{XY}$ (Å) | $0.047_0$ ±0.0016 | $0.047_4$ ±$0.003_3$ [12] | 0.08 ±0.02 [14] |
| $U_{YY}$ (Å) | 0.0892 ±0.0024 | $0.097_9$ ±$0.003_3$ [12] | 0.10 ±0.2 [14] |
| $\delta$ (Å) | 0.0022 ±0.0032 | — | — |

Table 1. Experimental molecular data for $SiCl_4$, $GeCl_4$ and $SnCl_4$.

for comparison, $SiCl_4$. The symmetry coordinates used were those of reference [4a]. For the normal frequencies of $GeCl_4$ and $SnCl_4$ we have measured the gas phase values of $\nu_3$ and $\nu_4$, but no gas phase values of the Raman active, infrared inactive, $\nu_1$ and $\nu_2$ have been reported. Hence we have used the values from liquid Raman [5] and tried to estimate the phase shifts and likely inaccuracies from those occuring in $SiCl_4$, $CCl_4$ and the $\nu_3$ and $\nu_4$ bands.

From the equation [2]

$$\zeta^{\alpha} = \boldsymbol{L}^{-1}\,\boldsymbol{C}^{\alpha}\,\boldsymbol{L}^{-1'}$$

and the defining equations of the $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices [6]:

$$\boldsymbol{G} = \boldsymbol{L}\,\boldsymbol{L}', \qquad \boldsymbol{F}^{-1} = \boldsymbol{L}\,\boldsymbol{\Lambda}^{-1}\,\boldsymbol{L}'$$

it is possible to derive an explicit equation between the Coriolis coupling and force constants [7]:

$$F_{33} + F_{44} + 2F_{34} = M_Y[(\lambda_3 - \lambda_4)\,\zeta_{44} + \tfrac{1}{2}\lambda_3 + \lambda_4] .$$

This used with the secular equation [6]:

$$|\boldsymbol{G}\,\boldsymbol{F} - \boldsymbol{E}\,\lambda| = 0$$

allows a full solution for the force constants of the $F_2$ species.

The results, giving values for the force constants, $\boldsymbol{L}$ matrix, mean amplitudes of vibration and Bastiansen-Morino shrinkage effect [8], are given for all three molecules in Table 2, whilst Tables 3 a, b, c show the variations of the $\boldsymbol{F}$, $\boldsymbol{L}$, $\boldsymbol{\Sigma}$ and $\boldsymbol{\zeta}$ matrix elements with each other over the region near the experimental values of $\zeta_{44}$.

| | $SiCl_4$ | $GeCl_4$ | $SnCl_4$ |
|---|---|---|---|
| $F_{11}$ ($A_1$) | 3.773 ±0.018 | 3.28 ±0.05 | 2.80 ±0.04 |
| $F_{22}$ (E) | 0.155 ±0.005 | 0.119 ±0.006 | 0.072 ±0.006 |
| $F_{33}$ ($F_2$) | 2.96 ±0.09 | 2.73 ±0.13 | 2.67 ±0.10 |
| $F_{34}$ ($F_2$) | $0.14_5$ ±0.03 | 0.13 ±0.08 | 0.23 ±0.11 |
| $F_{44}$ ($F_2$) | 0.236 ±0.005 | 0.170 ±0.003 | 0.120 ±0.011 |
| $L_{33}$ ($F_2$) | 0.2743 ±0.0004 | 0.2158 −0.0003 | 0.1974 ±0.0010 |
| $L_{34}$ ($F_2$) | 0.021 ±0.005 | 0.001 ±0.012 | −0.022 ±0.014 |
| $L_{43}$ ($F_2$) | −0.371 ±0.008 | −0.171 ±0.017 | −0.079 ±0.022 |
| $L_{44}$ ($F_2$) | 0.329 ±0.008 | 0.317 ±0.009 | 0.308 ±0.007 |
| (0°) | 0.0430 ±0.0001 | 0.0399 | 0.0398 |
| $U_{XY}$ (298°) | 0.0459 ±0.0002 | 0.0449 +0.0005 | 0.0472 ±0.0014 |
| (500°) | 0.0525 ±0.0002 | 0.0532 | 0.0569 |
| (0°) | 0.0615 ±0.0005 | 0.0639 | 0.0682 |
| $U_{YY}$ (298°) | 0.0883 ±0.0010 | 0.0990 ±0.0035 | 0.117 ±0.004 |
| (500°) | 0.1119 ±0.0023 | 0.125 | 0.150 |
| (0°) | 0.00177 | 0.00145 | 0.00162 |
| $\delta$ (298°) | 0.00311 ±0.00008 | 0.00377 ±0.00023 | 0.0057 ±0.0004 |
| (500°) | 0.00496 | 0.00605 | 0.0094 |

Table 2. Force field data for $SiCl_4$, $GeCl_4$ and $SnCl_4$. $F$ in mdynes/Å, $L$ in (a. m. u.)$^{-\frac{1}{2}}$, $U$ und $\delta$ in Å.

[4a] A. Müller, B. Krebs, S. J. Cyvin and E. Diemann, Z. Anorg. Allg. Chem., in press.

[4b] Mean of 6 determinations at (37 ± 2) °C using a Beckman IR 11 and Perkin Elmer 125 and 225 instruments.

[5] H. Siebert, Anwendung der Schwingungsspektroskopie in der Anorganischen Chemie, Springer-Verlag, Berlin 1966.

[6] E. B. Wilson, Jr., J. C. Decius and P. C. Cross, Molecular Vibrations, McGraw Hill, New York 1955.

[7] A. Müller and B. Krebs, Mol. Phys. **12**, 517 [1967].

[8] Y. Morino, S. J. Cyvin, K. Kuchitsu and T. Iijima, J. Chem. Phys. **36**, 1109 [1962].

| $F_{34}$ | $F_{33}$ | $F_{44}$ | $L_{33}$ | $L_{34}$ | $L_{43}$ | $L_{44}$ | $\zeta_{34}$ | $\zeta_{44}$ | | $\Sigma_{33}$ | $\Sigma_{34}$ | $\Sigma_{44}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| −0.0045 | 2.4549 | 0.2754 | 0.2707 | 0.0488 | −0.4029 | 0.2898 | 0.4758 | −0.3299 | M | 0.002582 | −0.001083 | 0.018008 |
| 0.0069 | 2.4992 | 0.2705 | 0.2712 | 0.0463 | −0.4002 | 0.2935 | 0.4865 | −0.3210 | | 0.002552 | −0.001153 | 0.018281 |
| 0.0182 | 2.5422 | 0.2660 | 0.2716 | 0.0438 | −0.3976 | 0.2971 | 0.4966 | −0.3123 | | 0.002525 | −0.001223 | 0.018546 |
| 0.0295 | 2.5840 | 0.2619 | 0.2720 | 0.0415 | −0.3950 | 0.3005 | 0.5062 | −0.3036 | | 0.002499 | −0.001293 | 0.018803 |
| 0.0409 | 2.6247 | 0.2582 | 0.2723 | 0.0392 | −0.3925 | 0.3038 | 0.5154 | −0.2951 | U,V | 0.002476 | −0.001363 | 0.019054 |
| 0.0522 | 2.6644 | 0.2547 | 0.2726 | 0.0370 | −0.3900 | 0.3070 | 0.5242 | −0.2866 | | 0.002455 | −0.001432 | 0.019299 |
| 0.0636 | 2.7031 | 0.2516 | 0.2729 | 0.0348 | −0.3875 | 0.3100 | 0.5326 | −0.2782 | A | 0.002435 | −0.001502 | 0.019537 |
| 0.0749 | 2.7411 | 0.2487 | 0.2731 | 0.0327 | −0.3851 | 0.3130 | 0.5407 | −0.2700 | | 0.002417 | −0.001572 | 0.019771 |
| 0.0863 | 2.7782 | 0.2460 | 0.2734 | 0.0307 | −0.3828 | 0.3159 | 0.5485 | −0.2618 | | 0.002401 | −0.001642 | 0.020000 |
| 0.0976 | 2.8146 | 0.2436 | 0.2736 | 0.0287 | −0.3804 | 0.3187 | 0.5559 | −0.2537 | | 0.002386 | −0.001712 | 0.020224 |
| 0.1089 | 2.8503 | 0.2413 | 0.2738 | 0.0267 | −0.3781 | 0.3214 | 0.5631 | −0.2456 | | 0.002372 | −0.001782 | 0.020444 |
| 0.1203 | 2.8854 | 0.2393 | 0.2740 | 0.0248 | −0.3759 | 0.3241 | 0.5701 | −0.2376 | F | 0.002360 | −0.001852 | 0.020660 |
| 0.1316 | 2.9199 | 0.2374 | 0.2741 | 0.0229 | −0.3736 | 0.3267 | 0.5767 | −0.2297 | | 0.002348 | −0.001922 | 0.020873 |
| 0.1430 | 2.9538 | 0.2358 | 0.2743 | 0.0210 | −0.3714 | 0.3292 | 0.5832 | −0.2218 | ζ | 0.002338 | −0.001992 | 0.021082 |
| 0.1543 | 2.9871 | 0.2343 | 0.2744 | 0.0192 | −0.3692 | 0.3317 | 0.5894 | −0.2140 | | 0.002329 | −0.002062 | 0.021287 |
| 0.1657 | 3.0200 | 0.2329 | 0.2745 | 0.0174 | −0.3670 | 0.3341 | 0.5955 | −0.2062 | | 0.002321 | −0.002131 | 0.021489 |
| 0.1770 | 3.0523 | 0.2317 | 0.2747 | 0.0156 | −0.3648 | 0.3365 | 0.6013 | −0.1985 | | 0.002313 | −0.002201 | 0.021689 |
| 0.1883 | 3.0842 | 0.2307 | 0.2747 | 0.0139 | −0.3627 | 0.3388 | 0.6069 | −0.1908 | | 0.002307 | −0.002271 | 0.021885 |
| 0.1997 | 3.1156 | 0.2298 | 0.2748 | 0.0122 | −0.3606 | 0.3410 | 0.6124 | −0.1832 | | 0.002301 | −0.002341 | 0.022078 |
| 0.2110 | 3.1467 | 0.2290 | 0.2749 | 0.0105 | −0.3585 | 0.3432 | 0.6177 | −0.1756 | | 0.002296 | −0.002411 | 0.022269 |
| 0.2224 | 3.1773 | 0.2283 | 0.2750 | 0.0088 | −0.3564 | 0.3454 | 0.6228 | −0.1681 | | 0.002292 | −0.002481 | 0.022457 |
| 0.2337 | 3.2075 | 0.2278 | 0.2750 | 0.0071 | −0.3543 | 0.3475 | 0.6278 | −0.1606 | | 0.002289 | −0.002551 | 0.022642 |
| 0.2451 | 3.2373 | 0.2274 | 0.2750 | 0.0055 | −0.3522 | 0.3496 | 0.6325 | −0.1531 | | 0.002286 | −0.002621 | 0.022823 |
| 0.2564 | 3.2668 | 0.2270 | 0.2751 | 0.0039 | −0.3502 | 0.3516 | 0.6371 | −0.1457 | | 0.002284 | −0.002691 | 0.022998 |
| 0.2677 | 3.2959 | 0.2268 | 0.2751 | 0.0023 | −0.3481 | 0.3534 | 0.6412 | −0.1383 | | 0.002283 | −0.002760 | 0.023154 |
| 0.2791 | 3.3247 | 0.2267 | 0.2751 | 0.0007 | −0.3461 | 0.3557 | 0.6463 | −0.1309 | L | 0.002282 | −0.002830 | 0.023369 |
| 0.2904 | 3.3531 | 0.2268 | 0.2751 | −0.0008 | −0.3441 | 0.3576 | 0.6504 | −0.1236 | | 0.002282 | −0.002900 | 0.023538 |

Table 3 a. Variations of the $F$, $L$, $\zeta$ and $\Sigma$ matrix elements for $SiCl_4$ $F$ in mdynes/Å; $L$ in (a. m. u.)$^{-\frac{1}{2}}$, $\Sigma$ in Å$^2$. Approximate positions of various solutions are marked: M=M. V. F. F.; L=L matrix method; U=U. B. F. F.; A=from mean amplitudes; V=Vol'kenshtein field; $\zeta$=from Coriolis constant; F=Fadini „Verfahren".

| $F_{34}$ | $F_{33}$ | $F_{44}$ | $L_{33}$ | $L_{34}$ | $L_{43}$ | $L_{44}$ | $\zeta_{34}$ | $\zeta_{44}$ | | $\Sigma_{33}$ | $\Sigma_{34}$ | $\Sigma_{44}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| −0.0066 | 2.4857 | 0.1794 | 0.2148 | 0.0209 | −0.2002 | 0.2997 | 0.6944 | −0.0337 | M | 0.002244 | −0.000396 | 0.024664 |
| 0.0052 | 2.5090 | 0.1778 | 0.2150 | 0.0190 | −0.1976 | 0.3014 | 0.6992 | −0.0216 | | 0.002228 | −0.000506 | 0.024880 |
| 0.0170 | 2.5319 | 0.1763 | 0.2151 | 0.0172 | −0.1950 | 0.3031 | 0.7038 | −0.0096 | | 0.002214 | −0.000616 | 0.025092 |
| 0.0289 | 2.5542 | 0.1749 | 0.2153 | 0.0154 | −0.1924 | 0.3047 | 0.7081 | 0.0024 | | 0.002202 | −0.000725 | 0.025299 |
| 0.0407 | 2.5762 | 0.1738 | 0.2154 | 0.0136 | −0.1898 | 0.3063 | 0.7121 | 0.0143 | | 0.002191 | −0.000835 | 0.025502 |
| 0.0525 | 2.5977 | 0.1727 | 0.2155 | 0.0118 | −0.1873 | 0.3079 | 0.7159 | 0.0261 | F | 0.002182 | −0.000945 | 0.025701 |
| 0.0644 | 2.6187 | 0.1719 | 0.2156 | 0.0100 | −0.1848 | 0.3094 | 0.7195 | 0.0379 | | 0.002174 | −0.001054 | 0.025896 |
| 0.0762 | 2.6394 | 0.1712 | 0.2157 | 0.0083 | −0.1823 | 0.3109 | 0.7228 | 0.0496 | | 0.002167 | −0.001164 | 0.026086 |
| 0.0880 | 2.6596 | 0.1706 | 0.2157 | 0.0065 | −0.1798 | 0.2123 | 0.7259 | 0.0612 | | 0.002162 | −0.001274 | 0.026272 |
| 0.0999 | 2.6795 | 0.1702 | 0.2158 | 0.0048 | −0.1773 | 0.3137 | 0.7287 | 0.0727 | | 0.002158 | −0.001383 | 0.026451 |
| 0.1117 | 2.6990 | 0.1699 | 0.2158 | 0.0031 | −0.1748 | 0.3150 | 0.7312 | 0.0842 | U,A | 0.002155 | −0.001493 | 0.026617 |
| 0.1235 | 2.7182 | 0.1697 | 0.2158 | 0.0015 | −0.1724 | 0.3158 | 0.7323 | 0.0956 | L,ζ | 0.002153 | −0.001603 | 0.026791 |
| 0.1354 | 2.7370 | 0.1696 | 0.2158 | −0.0002 | −0.1699 | 0.3169 | 0.7365 | 0.1070 | | 0.002153 | −0.001713 | 0.026967 |
| 0.1472 | 2.7554 | 0.1697 | 0.2158 | −0.0019 | −0.1675 | 0.3187 | 0.7374 | 0.1183 | | 0.002154 | −0.001822 | 0.027093 |
| 0.1590 | 2.7735 | 0.1699 | 0.2158 | −0.0035 | −0.1650 | 0.3203 | 0.7401 | 0.1295 | | 0.002156 | −0.001932 | 0.027313 |
| 0.1709 | 2.7913 | 0.1702 | 0.2157 | −0.0051 | −0.1626 | 0.3216 | 0.7420 | 0.1407 | | 0.002158 | −0.002042 | 0.027488 |
| 0.1827 | 2.8088 | 0.1707 | 0.2157 | −0.0068 | −0.1602 | 0.3228 | 0.7436 | 0.1518 | | 0.002162 | −0.002151 | 0.027654 |
| 0.1945 | 2.8259 | 0.1712 | 0.2156 | −0.0084 | −0.1578 | 0.3240 | 0.7450 | 0.1629 | | 0.002167 | −0.002261 | 0.027815 |
| 0.2063 | 2.8428 | 0.1719 | 0.2156 | −0.0100 | −0.1554 | 0.3252 | 0.7462 | 0.1739 | | 0.002174 | −0.002371 | 0.027973 |
| 0.2182 | 2.8593 | 0.1726 | 0.2155 | −0.0115 | −0.1530 | 0.3263 | 0.7473 | 0.1849 | | 0.002181 | −0.002480 | 0.028127 |
| 0.2300 | 2.8755 | 0.1735 | 0.2154 | −0.0131 | −0.1506 | 0.3274 | 0.7481 | 0.1958 | | 0.002189 | −0.002590 | 0.028278 |
| 0.2418 | 2.8915 | 0.1745 | 0.2153 | −0.0147 | −0.1482 | 0.3285 | 0.7488 | 0.2067 | | 0.002198 | −0.002700 | 0.028426 |
| 0.2537 | 2.9072 | 0.1755 | 0.2152 | −0.0162 | −0.1459 | 0.3296 | 0.7494 | 0.2175 | | 0.002208 | −0.002810 | 0.028571 |
| 0.2655 | 2.9225 | 0.1767 | 0.2151 | −0.0178 | −0.1435 | 0.3306 | 0.7498 | 0.2283 | | 0.002219 | −0.002919 | 0.028714 |
| 0.2773 | 2.9376 | 0.1780 | 0.2149 | −0.0193 | −0.1411 | 0.3316 | 0.7500 | 0.2390 | V | 0.002230 | −0.003029 | 0.028854 |
| 0.2892 | 2.9525 | 0.1794 | 0.2148 | −0.0208 | −0.1387 | 0.3326 | 0.7501 | 0.2497 | | 0.002243 | −0.003139 | 0.028992 |
| 0.3010 | 2.9670 | 0.1808 | 0.2146 | −0.0224 | −0.1364 | 0.3336 | 0.7500 | 0.2603 | | 0.002257 | −0.003248 | 0.029127 |

Table 3 b. Variations of the $F$, $L$, $\zeta$ and $\Sigma$ matrix elements for $GeCl_4$ (see table 3 a for details).

| $F_{34}$ | $F_{33}$ | $F_{44}$ | $L_{33}$ | $L_{34}$ | $L_{43}$ | $L_{44}$ | $\zeta_{34}$ | $\zeta_{44}$ | | $\Sigma_{33}$ | $\Sigma_{34}$ | $\Sigma_{44}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| −0.0061 | 2.4258 | 0.1097 | 0.1984 | 0.0092 | −0.1267 | 0.2920 | 0.7428 | 0.1462 | M,U,F | 0.002202 | −0.000190 | 0.038895 |
| 0.0098 | 2.4463 | 0.1088 | 0.1985 | 0.0070 | −0.1235 | 0.2934 | 0.7449 | 0.1626 | | 0.002188 | −0.000437 | 0.039209 |
| 0.0257 | 2.4661 | 0.1082 | 0.1985 | 0.0048 | −0.1203 | 0.2947 | 0.7466 | 0.1790 | | 0.002178 | −0.000684 | 0.039507 |
| 0.0417 | 2.4853 | 0.1078 | 0.1986 | 0.0026 | −0.1171 | 0.2958 | 0.7476 | 0.1952 | | 0.002172 | −0.000931 | 0.039766 |
| 0.0576 | 2.5039 | 0.1076 | 0.1986 | 0.0005 | −0.1139 | 0.2969 | 0.7490 | 0.2114 | L | 0.002169 | −0.001178 | 0.040054 |
| 0.0735 | 2.5219 | 0.1077 | 0.1986 | −0.0016 | −0.1107 | 0.2979 | 0.7496 | 0.2274 | | 0.002170 | −0.001425 | 0.040342 |
| 0.0895 | 2.5393 | 0.1079 | 0.1986 | −0.0037 | −0.1075 | 0.2995 | 0.7498 | 0.2432 | | 0.002174 | −0.001673 | 0.040630 |
| 0.1054 | 2.5562 | 0.1084 | 0.1985 | −0.0058 | −0.1044 | 0.3007 | 0.7499 | 0.2590 | | 0.002182 | −0.001920 | 0.040909 |
| 0.1213 | 2.5725 | 0.1092 | 0.1984 | −0.0079 | −0.1012 | 0.3018 | 0.7496 | 0.2747 | | 0.002193 | −0.002167 | 0.041167 |
| 0.1373 | 2.5882 | 0.1101 | 0.1983 | −0.0100 | −0.0981 | 0.3029 | 0.7490 | 0.2903 | | 0.002208 | −0.002414 | 0.041414 |
| 0.1532 | 2.6035 | 0.1112 | 0.1982 | −0.0120 | −0.0949 | 0.3039 | 0.7480 | 0.3057 | | 0.002225 | −0.002661 | 0.041651 |
| 0.1691 | 2.6182 | 0.1126 | 0.1981 | −0.0140 | −0.0918 | 0.3048 | 0.7467 | 0.3211 | | 0.002246 | −0.002908 | 0.041880 |
| 0.1851 | 2.6324 | 0.1141 | 0.1979 | −0.0161 | −0.0887 | 0.3057 | 0.7451 | 0.3363 | | 0.002270 | −0.003155 | 0.042101 |
| 0.2010 | 2.6461 | 0.1158 | 0.1978 | −0.0181 | −0.0856 | 0.3066 | 0.7432 | 0.3515 | | 0.002297 | −0.003402 | 0.042314 |
| 0.2169 | 2.6593 | 0.1178 | 0.1976 | −0.0201 | −0.0825 | 0.3075 | 0.7410 | 0.3666 | | 0.002327 | −0.003649 | 0.042519 |
| 0.2329 | 2.6720 | 0.1199 | 0.1974 | −0.0221 | −0.0793 | 0.3083 | 0.7385 | 0.3815 | | 0.002360 | −0.003896 | 0.042716 |
| 0.2488 | 2.6842 | 0.1222 | 0.1971 | −0.0241 | −0.0762 | 0.3091 | 0.7356 | 0.3964 | | 0.002395 | −0.004143 | 0.042905 |
| 0.2647 | 2.6959 | 0.1247 | 0.1969 | −0.0261 | −0.0731 | 0.3098 | 0.7326 | 0.4112 | | 0.002434 | −0.004390 | 0.043087 |
| 0.2807 | 2.7072 | 0.1274 | 0.1966 | −0.0280 | −0.0700 | 0.3106 | 0.7292 | 0.4258 | | 0.002476 | −0.004637 | 0.043261 |
| 0.2966 | 2.7179 | 0.1303 | 0.1963 | −0.0300 | −0.0669 | 0.3112 | 0.7255 | 0.4404 | | 0.002521 | −0.004884 | 0.043428 |
| 0.3125 | 2.7282 | 0.1333 | 0.1960 | −0.0320 | −0.0638 | 0.3119 | 0.7215 | 0.4549 | | 0.002568 | −0.005131 | 0.043587 |
| 0.3285 | 2.7380 | 0.1366 | 0.1957 | −0.0339 | −0.0606 | 0.3125 | 0.7173 | 0.4693 | | 0.002619 | −0.005378 | 0.043739 |
| 0.3444 | 2.7473 | 0.1400 | 0.1953 | −0.0359 | −0.0575 | 0.3131 | 0.7128 | 0.4836 | | 0.002672 | −0.005625 | 0.043884 |
| 0.3603 | 2.7561 | 0.1437 | 0.1950 | −0.0378 | −0.0544 | 0.3137 | 0.7079 | 0.4978 | | 0.002728 | −0.005872 | 0.044021 |
| 0.3763 | 2.7645 | 0.1475 | 0.1946 | −0.0398 | −0.0512 | 0.3142 | 0.7028 | 0.5119 | | 0.002787 | −0.006119 | 0.044151 |
| 1.0455 | 2.5199 | 0.5394 | 0.1494 | −0.1309 | 0.1110 | 0.2984 | 0.1329 | 0.9881 | | 0.008864 | −0.016496 | 0.040359 |
| 1.0614 | 2.4824 | 0.5610 | 0.1465 | −0.1341 | 0.1176 | 0.2959 | 0.1003 | 0.9933 | | 0.009200 | −0.016743 | 0.039776 |
| 1.0773 | 2.4389 | 0.5950 | 0.1432 | −0.1376 | 0.1247 | 0.2929 | 0.0643 | 0.9972 | | 0.009571 | −0.016990 | 0.039103 |
| 1.0933 | 2.3874 | 0.6121 | 0.1394 | −0.1415 | 0.1326 | 0.2894 | 0.0235 | 0.9996 | V | 0.009992 | −0.017237 | 0.038305 |
| 1.1092 | 2.3235 | 0.6441 | 0.1347 | −0.1459 | 0.1419 | 0.2850 | −0.0248 | 0.9996 | | 0.010487 | −0.017484 | 0.037313 |
| 1.1251 | 2.2359 | 0.6852 | 0.1285 | −0.1514 | 0.1536 | 0.2788 | −0.0872 | 0.9949 | | 0.011125 | −0.017731 | 0.035954 |

Table 3 c. Variations of the $F$, $L$, $\zeta$ and $\Sigma$ matrix elements for $SnCl_4$ (see table 3 a for details).

## Germanium Tetrachloride

Various approximate force fields have been used to fix the $F_2$ species constants of $GeCl_4$, Table 4 gives several of them: the M.V.F.F. ($F_{34}=0$) is seen to be well outside the experimental error; the $L$ matrix approximation of MÜLLER ($L_{34}=0$) [9] is seen in this case to be excellent, and both the U.B.F.F.[10] and „Verfahren der nächsten Lösung" of FADINI [11], although using somewhat different frequency data, are in good agreement. There have been other attempts at fixing the exact field: MORINO et al. [12] used experimental mean amplitudes and their results are in good agreement with ours, although their error limits are much higher, whilst CHANTRY and WOODWARD [13] used Vol'kenshtein's theory of absolute Raman intensities but their results are quite outside the range of the present determination, especially with respect to the interaction constant $F_{34}$.

| | U.B.F.F.[10] | M.V.F.F. | $L_{34}=0$ | Fadini [11] | Vol'kenshtein [13] | from $\zeta_{44}$ | from $U$-values [12] |
|---|---|---|---|---|---|---|---|
| $F_{33}$ | 2.66 | 2.50 | 2.73 | 2.57 | 2.93 | 2.73 ±0.13 | 2.63±0.30 |
| $F_{34}$ | 0.11 | 0 | 0.13 | 0.06 | 0.30 | 0.13 ±0.08 | 0.12±0.20 |
| $F_{44}$ | 0.18 | 0.178 | 0.170 | 0.18 | 0.183 | 0.170±0.003 | 0.18±0.01 |

Table 4. Different force fields for the $F_2$ species of $GeCl_4$ in mdynes/Å.

[9] A. MÜLLER, Z. Phys. Chem. Leipzig, in press. — C. J. PEACOCK and A. MÜLLER, J. Mol. Spectr., in press.
[10] A. MÜLLER and B. KREBS, J. Mol. Spectr. **24**, 180 [1967].
[11] B. KREBS, A. MÜLLER and A. FADINI, J. Mol. Spectr. **24**, 198 [1967].
[12] Y. MORINO, Y. NAKAMURA and T. IIJIMA, J. Chem. Phys. **32**, 643 [1960].
[13] C. W. CHANTRY and L. A. WOODWARD, Trans. Faraday Soc. **56**, 1110 [1960].

### Tin Tetrachloride

In Table 5 various other values of the force constants for $SnCl_4$ are given, it being seen that the approximations fall mainly together, but well outside the present determination; the U. B. F. F.[10], Fadini „Verfahren“[11], and M.V. F. F. giving almost the same values, the $L$ matrix method being in between these and the Coriolis fixed values; the VOL'KENSHTEIN method[13] gives a vastely different field with inconceivably large values for $F_{34}$ and $F_{44}$ (note also the potential energy distribution in $\nu_3$ where $F_{33}$ and $F_{34}$ contribute equally (43.2 and 43.5%), showing $F_{34}$ to be far too large). However this field does agree with the experimental mean amplitudes[14].

Now for both $SiCl_4$ and $GeCl_4$ the approximate methods, especially the U. B. F. F. and Fadini „Verfahren“, work well, and in general it is found that the higher the mass ratio, $M_X : M_Y$, the better the approximations become, for the interaction term $F_{34}$ becomes smaller. It would appear that the approximate methods ought work well for $SnCl_4$.

The VOL'KENSHTEIN field agrees with both experimental mean amplitudes whilst our determination only agrees with $U_{YY}$. Now it is well known that the force field is not very dependent on $U_{XY}$ (see e. g. 9 or 15), but it is on $U_{YY}$. Also CYVIN[15], from comparison of the usual values of mean amplitudes has concluded that $U_{XY}$ for $SnCl_4$ is much too high. The odd results given by the VOL'KENSHTEIN field and the above lead us to suggest that the experimental value of $U_{XY}$ is quite wrong.

The mean amplitudes calculated from the approximations (e. g. FADINI „Verfahren“ at 298°: $U_{XY}$ 0.0459, $U_{YY}$ 0.0125) are within the limits calculated from the Coriolis constant, although the force fields are rather different. This is due, for $U_{XY}$, to the two solutions lying on opposite sides of the minimum in $U_{XY}$ (occuring when $L_{34}=0$), and for $U_{YY}$ to the error on $\nu_2$ increasing the error enough to encompass the approximate values. It may thus be that mean amplitudes are not sensitive enough to discriminate between the present force field and the approximate ones, although there is a significant difference between them, easily shown by $\zeta_{44}$ calculated from the Fadini „Verfahren“, it being 0.14, which would be a PR separation of 9 $cm^{-1}$ (instead of the experimental $6.6 \pm 1.1$ $cm^{-1}$). It may be that $SnCl_4$ is a peculiar molecule for which the approximations fail, or that the band contours are somehow perturbed and a false separation measured. Without further evidence we cannot claim any definite accuracy, therefore, for our force field.

### Conclusion

The Coriolis constants measured for $SiCl_4$, $GeCl_4$ and $SnCl_4$ well demonstrate the possibilities and pitfalls of using this method to determine accurate force fields, mean amplitudes etc.

$SiCl_4$ gave an excellent spectrum, an accurate Coriolis constant, and hence an accurate force field. Mean amplitudes calculated by this method are much more accurate than the experimental values ($U_{XY}$ 8 times, $U_{YY}$ $2\frac{1}{2}$ times, most of the error being from the illdefined $\nu_2$, which if known to $\pm 0.5$ $cm^{-1}$ would allow the accuracy to be improved to 8 times the experimental), and similarly the Bastiansen-Morino shrinkage effect is far more accurately defined.

$GeCl_4$ gave not such a good spectrum, and hence quite a large error on the Coriolis constant, but it is of note that the force field does not change much over the range of probable values of $\zeta_{44}$: $F_{33}$ being defined to within 5%, $F_{44}$ even more accurately and only $F_{34}$ having a large percentage error. This appears true of most heavier molecules, that although the Coriolis constant cannot be measured very accurately the force field is not very sensitive to it.

| | U. B. F. F.[10] | M. V. F. F. | $L_{34}=0$ | Fadini[11] | Vol'kenshtein[13] | from $\zeta_{44}$ |
|---|---|---|---|---|---|---|
| $F_{33}$ | 2.45 | 2.43 | 2.51 | 2.41 | 2.30 | 2.67 ±0.10 |
| $F_{34}$ | 0.05 | 0 | 0.06 | 0.02 | 1.06 | 0.23 ±0.11 |
| $F_{44}$ | 0.12 | 0.109 | 0.108 | 0.12 | 0.61 | 0.120±0.011 |

Table 5. Different force fields for the $F_2$ species of $SnCl_4$ in mdynes/Å.

[14] R. L. LIVINGSTONE and C. N. RAO, J. Chem. Phys. **30**, 339 [1959] and private communication cited in: D. A. LONG and J. Y. H. CHAU, Trans. Faraday. Soc. **58**, 2328 [1962].

[15] S. J. CYVIN, Mean Square Amplitudes and Molecular Vibrations. Universitetsforlaget, Oslo, in press.

Another interesting point is that such an inaccurate Coriolis constant yields as accurate a mean amplitude $U_{YY}$ as the experimental value (and even then 20% of the error comes from that on $\nu_2$), whilst a far better value for $U_{XY}$, which is not very sensitive to the force field, is obtained. As the error on $\nu_2$ gets added into the $F_2$ force field when calculating this from experimental mean amplitudes, it is seen that the Coriolis constant can here give a much better defined force field than mean amplitudes.

Finally $SnCl_4$ shows the drawbacks of the method, the force field being possibly incorrect: yet not by much for it is quite insensitive to the Coriolis coupling here, the value obtained being much better than the, almost certainly, wildly incorrect Vol'kenshtein field, or that from the, albeit very inaccurate, mean amplitudes.

It would thus appear that if Coriolis constants can be measured they are the best method of defining the force field, but they may be measured incorrectly in some difficult cases. Certainly a further measurement of the mean amplitudes of $SnCl_4$ is much needed and might help clear up the confusion over the force field of this molecule.

We wish to thank Prof. O. GLEMSER for his generous support and Prof. W. LÜTTKE, who allowed us to use his Perkin Elmer instruments.

# Das Kombinationsschwingungsspektrum von Gips im Bereich von 10000—1200 $cm^{-1}$

V. HOHLER und H. D. LUTZ

Institut für Physikalische Chemie, Universität Freiburg i. Br.

(Z. Naturforsch. **23 a**, 708—715 [1968]; eingegangen am 15. Februar 1968)

The IR-spectrum of gypsum ($CaSO_4 \cdot 2\,H_2O$) in the frequency range from 10 000 to 1200 $cm^{-1}$ has been investigated with polarized light at room temperature. Between 3700 and 1200 $cm^{-1}$, the measurements confirm the data of HASS and SUTHERLAND and as well as those of SCHAAK derived from IR and reflection measurements. The IR-spectrum shows a great number of bands, most of which can be assigned to combination and fundamental vibrations in terms of normal vibrations of the water molecules and the sulfate ions. The influence of the lattice vibrations is briefly discussed. The existence of hydrogen bonds between the water molecules and the sulfate ions gives rise to combinations of fundamental vibrations of both complexes.

Der monokline Gips ist seit vielen Jahren Gegenstand zahlreicher wissenschaftlicher Arbeiten gewesen [1–4], wobei in den spektroskopischen Arbeiten neueren Datums von HASS und SUTHERLAND [5] und SCHAACK [6, 7] vor allem den inneren Schwingungen der $SO_4$-Ionen und der auf Gitterplätzen definiert eingebauten $H_2O$-Moleküle besondere Aufmerksamkeit geschenkt wurde.

Die genannten Autoren sind sich darüber einig, daß der definierte Einbau des Kristallwassers sowie die Wechselwirkung der $H_2O$-Moleküle mit dem Gitter den H-Brückenbindungen zuzuschreiben ist, die zwischen den H-Atomen der Wassermoleküle und den O-Atomen der tetraedrischen $SO_4$-Ionen bestehen. Diese Wechselwirkung äußert sich spektroskopisch sowohl in einer starken Verbreiterung bestimmter $H_2O$-Banden infolge der relativ starken Ankopplung an die Gitterschwingungen als auch in einer teilweise sehr starken Temperaturabhängigkeit der Bandenbreiten und -intensitäten, wie dies von SCHAACK [6] beobachtet wurde und durch den speziellen Aufbau des Gitters erklärt werden kann.

Außer den Grundfrequenzen der inneren Schwingungen wurden von verschiedenen Autoren [5, 6] in Reflexion und im Raman-Effekt auch einige Frequenzen äußerer Schwingungen gemessen, wobei allerdings erwähnt werden muß, daß die äußeren Schwingungen nicht in der Vollständigkeit bekannt sind, wie dies für die inneren Schwingungen der $SO_4$-Ionen und $H_2O$-Moleküle der Fall ist.

Die Absicht dieser Arbeit ist es, das Spektrum der Kombinationsschwingungen näher zu untersu-

[1] C. SCHAEFER u. K. SCHUBERT, Ann. Phys. (4) **50**, 283 [1916].
[2] T. LIEBISCH u. RUBENS, Sitz.-Ber. Preuss. Akad. Wiss., Berlin **1**, 198 [1919].
[3] J. LOUISFERT, J. Chim. Phys. **15** 44 [1948].
[4] M. ATOJI u. R. E. RUNDLE, J. Chem. Phys. **29**, 1306 [1958].
[5] E. HASS u. M. SUTHERLAND, Proc. Roc. Soc. London **236 A**, 467 [1956].
[6] G. SCHAACK, Phys. kondens. Mat. **1**, 245 [1963].
[7] G. SCHAACK, Z. Phys. **176**, 67 [1963].