

Table 2. Bastiansen-Morino shrinkage effects for six octahedral hexafluorides (Å units).

Molecule	Nonlinear FF $\begin{pmatrix} X \\ F \dots F \end{pmatrix}$	Linear FF (F-X-F)
SF ₆	0.000644 ^a 0.000677 ^b	0.002071 0.002520
SeF ₆	0.000560 0.000721	0.002132 0.005431
TeF ₆	0.000601 0.001056	0.002385 0.003305
MoF ₆	0.001100 0.001843	0.002666 0.004897
WF ₆	0.000591 0.001213	0.002327 0.003412
UF ₆	0.000812 0.000868	0.003122 0.006977

^{a,b} See footnote to Table 1.

for sulphur hexafluoride along with the values for the five additional hexafluorides here considered.

1. Cyvin, S. J. *Kgl. Norske Videnskab. Selskabs Skrifter* **1959** No. 2.
2. Bastiansen, O. and Trøtteberg, M. *Acta Cryst.* **13** (1960) 1108; Morino, Y. *Acta Cryst.* **13** (1960) 1107; Morino, Y., Cyvin, S. J., Kuchitsu, K. and Iijima, T. *J. Chem. Phys.* **36** (1962) 1109; Cyvin, S. J. *Tidsskr. Kjemi Bergvesen Met.* **22** (1962) 44, 73.
3. Bye, B. H. and Cyvin, S. J.; Cyvin, S. J. and Meisingseth, E. *To be published.*
4. Pistorius, C. W. F. T. *J. Chem. Phys.* **29** (1958) 1328.
5. Gaunt, J. *Trans. Faraday Soc.* **49** (1955) 1122.
6. Claassen, H. H. *J. Chem. Phys.* **30** (1959) 968.
7. Gaunt, J. *Trans. Faraday Soc.* **50** (1954) 546.

Received October 22, 1962.

Coriolis C Matrix and the Mean-Square Amplitude Σ Matrix in the Problem of Rotation-Vibration Interaction

S. J. CYVIN and L. KRISTIANSEN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The "Coriolis" C matrix method developed by Meal and Polo¹ will probably become the standard method for studying Coriolis interaction in rotating-vibrating molecules. The method has been applied to specific molecular models by several authors², and has also been considered in general by Mills³.

The Coriolis interaction is closely connected with the force constants of a molecule. In fact the Coriolis coefficients (ζ -values) may be calculated through the L matrix ($S = LQ$), which is obtainable from the force constants. One has

$$\zeta^{\alpha} = L^{-1} C^{\alpha} \widetilde{L}^{-1} \quad (1)$$

using the conventional symbols¹. Here the C^{α} matrix may be defined by

$$C^{\alpha} = B M^{\alpha} \widetilde{B} \quad (2)$$

We prefer to think of the B matrix as associated with the usual cartesian displacements ($S = BX$) rather than the mass-weighted coordinates $q_i = m_i^{-1/2} x_i$. Then the M^{α} matrix must be defined in the following way. It consists of the blocks $M_1^{\alpha}, M_2^{\alpha}, \dots, M_N^{\alpha}$ ($N =$ number of atoms) along the main diagonal, which are defined for $\alpha = x, y, z$ by

$$M_1^x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \mu_i \\ 0 & -\mu_i & 0 \end{bmatrix}$$

$$M_1^y = \begin{bmatrix} 0 & 0 & -\mu_i \\ 0 & 0 & 0 \\ \mu_i & 0 & 0 \end{bmatrix}$$

$$M_1^z = \begin{bmatrix} 0 & \mu_i & 0 \\ -\mu_i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

μ_i denotes as usual the inverse mass of the i -th atom. Our eqn. (2) appears to be a slight modification of eqn. (II-3) from the ingenious work of Meal and Polo¹. Our equation shows more closely the analogy with the definition of the G matrix, which usually is written in the form

Appendix: Summary of relations containing eqns. (4)–(11) along with several alternative forms.

$$\begin{array}{ll}
 (1) & \zeta^{\alpha} = \widetilde{L} G^{-1} C^{\alpha} \widetilde{L}^{-1} \quad |G^{-1} C^{\alpha} - \sigma E| \equiv |\zeta^{\alpha} - \sigma E| = 0 \\
 (2) & A \zeta^{\alpha} = \widetilde{L} F C^{\alpha} \widetilde{L}^{-1} \quad |F C^{\alpha} - \gamma E| \equiv |A \zeta^{\alpha} - \gamma E| = 0 \\
 (3) & A^{-1} \zeta^{\alpha} = \widetilde{L} \Sigma^{-1} C^{\alpha} \widetilde{L}^{-1} \quad \text{No practical importance (?)} \\
 (1') & \zeta^{\alpha} = L^{-1} C^{\alpha} G^{-1} \quad |C^{\alpha} G^{-1} - \sigma' E| \equiv |\zeta^{\alpha} - \sigma' E| = 0 \\
 (2') & \zeta^{\alpha} A = L^{-1} C^{\alpha} F L \quad |C^{\alpha} F - \gamma' E| \equiv |\zeta^{\alpha} A - \gamma' E| = 0 \\
 (3') & \zeta^{\alpha} A^{-1} = L^{-1} C^{\alpha} \Sigma^{-1} L \quad \text{No practical importance (?)} \\
 (1'') & \zeta^{\alpha} = L^{-1} C^{\alpha} G^{-1} L \quad \text{Identical with (1')} \\
 (2'') & A^{-1} \zeta^{\alpha} = L^{-1} F^{-1} G^{-1} C^{\alpha} G^{-1} L \\
 (3'') & A \zeta^{\alpha} = L^{-1} \Sigma G^{-1} C^{\alpha} G^{-1} L \quad |F^{-1} G^{-1} C^{\alpha} G^{-1} - \gamma'' E| \equiv |A^{-1} \zeta^{\alpha} - \gamma'' E| = 0 \\
 (1''') & \zeta^{\alpha} = L^{-1} C^{\alpha} G^{-1} L \quad |L \Sigma G^{-1} C^{\alpha} G^{-1} - \kappa E| \equiv |A \zeta^{\alpha} - \kappa E| = 0 \\
 (2''') & \zeta^{\alpha} A^{-1} = L^{-1} C^{\alpha} G^{-1} F^{-1} G^{-1} L \\
 (3''') & \zeta^{\alpha} A = L^{-1} C^{\alpha} G^{-1} \Sigma G^{-1} L \quad |C^{\alpha} G^{-1} F^{-1} G^{-1} - \gamma''' E| \equiv |\zeta^{\alpha} A^{-1} - \gamma''' E| = 0 \\
 & |C^{\alpha} G^{-1} \Sigma G^{-1} - \kappa' E| \equiv |\zeta^{\alpha} A - \kappa' E| = 0
 \end{array}$$

$$G = B \mu \widetilde{B} \quad (3)$$

Here the μ matrix may be defined in terms of the diagonal blocks $\mu_1, \mu_2, \dots, \mu_N$, where

$$\mu_i = \begin{bmatrix} \mu_i & 0 & 0 \\ 0 & \mu_i & 0 \\ 0 & 0 & \mu_i \end{bmatrix}$$

Cyvin⁴ has introduced the Σ matrix (mean-square amplitude matrix), and proved it to be equivalent with the force constant matrix. Thus the L matrix may be obtained from the complete Σ matrix, as well as the force constant matrix. It seems, therefore, very reasonable to seek for some relations between ζ -values and the Σ -matrix elements, similar to the existing relations between ζ -values and the force constants. Such relations have been evaluated in this work.

By combining eqn. (1) with $E = \widetilde{L} G^{-1} L$ and $A = \widetilde{L} F L$, respectively, one obtains the relations of Meal and Polo¹, viz.

$$\zeta^{\alpha} = \widetilde{L} G^{-1} C^{\alpha} \widetilde{L}^{-1} \quad (4)$$

$$A \zeta^{\alpha} = \widetilde{L} F C^{\alpha} \widetilde{L}^{-1} \quad (5)$$

from which the following characteristic equations have been deduced¹

$$|G^{-1} C^{\alpha} - \sigma E| \equiv |\zeta^{\alpha} - \sigma E| = 0 \quad (6)$$

$$|F C^{\alpha} - \gamma E| \equiv |A \zeta^{\alpha} - \gamma E| = 0 \quad (7)$$

It is true that an analogous relation may be obtained from $A^{-1} = \widetilde{L} \Sigma^{-1} L$ combined

with (1). This relation would contain Σ^{-1} and is assumed not to have practical importance, at least before any clear physical significance is found for the inverse Σ matrix. Hence we proceeded in an other way, com-

binning $A = L^{-1} \Sigma \widetilde{L}^{-1}$ with (1). In addition we utilized the well-known relation $G^{-1} = \widetilde{L}^{-1} L^{-1}$ and obtained the result

$$A \zeta^{\alpha} = L^{-1} \Sigma G^{-1} C^{\alpha} G^{-1} L \quad (8)$$

This is a similarity transformation. Hence the $A \zeta^{\alpha}$ and $\Sigma G^{-1} C^{\alpha} G^{-1}$ matrices have identical characteristic values, and consequently

$$|\Sigma G^{-1} C^{\alpha} G^{-1} - \kappa E| \equiv |A \zeta^{\alpha} - \kappa E| = 0 \quad (9)$$

The relation has been applied to the case of planar symmetrical XY_3 molecules, and has proved its usefulness⁵.

We also wish to point out that a relation of the form (9) exists for the inverse F matrix. One has

$$A^{-1} \zeta^{\alpha} = L^{-1} F^{-1} G^{-1} C^{\alpha} G^{-1} L \quad (10)$$

and consequently

$$|F^{-1} G^{-1} C^{\alpha} G^{-1} - \gamma'' E| \equiv |A^{-1} \zeta^{\alpha} - \gamma'' E| = 0 \quad (11)$$

1. Meal, J. H. and Polo, S. R. *J. Chem. Phys.* **24** (1956) 1119, 1126.
2. Günthard, H. H., Lord, R. C. and McCubbin, T. K., Jr. *J. Chem. Phys.* **25** (1956) 768; Nakagawa, I. and Shimanouchi, T. *Spectrochim. Acta* **18** (1962) 513.

3. Mills I. M. *Spectrochim. Acta* **16** (1960) 35; *J. Mol. Spectr.* **5** (1960) 334.
4. Cyvin, S. J. *Acta Chem. Scand.* **13** (1959) 2135; *Spectrochim. Acta* **15** (1959) 828.
5. Kristiansen, L. and Cyvin, S. J. *To be published.*

Received October 22, 1962.

On the Mechanism of Rhodanese Inhibition by Sulfite and Cyanide

BO SÖRBO

Nobel Medical Institute, Biochemical Department, Stockholm, Sweden

The inhibition of rhodanese by cyanide¹ or sulfite² has been interpreted as being due to a reaction of the inhibitor with a disulfide bond in the enzyme^{3,4}. However, Green and Westley⁵ have recently observed that the inhibition of rhodanese by cyanide was more rapid in dilute than in concentrated enzyme solutions, which would not be expected if the inhibition was due to a direct reaction of the inhibitor with the enzyme. Furthermore they found that crystalline rhodanese contained labile sulfur, which could be exchanged with the outer sulfur atom of thiosulfate or removed from the enzyme by incubation with cyanide or sulfite. The sulfur-rhodanese complex was formed when the free enzyme reacted with a sulfur donor, *e.g.* thiosulfate, and thus represents an intermediate in the rhodanese reaction. Since thiosulfate is present in some of the purification steps used for the preparation of crystalline rhodanese^{6,7}, the latter is obtained in the form of this sulfur complex. Green and Westley suggested that either cyanide or sulfite inactivates rhodanese by removing the labile sulfur from the enzyme; this treatment yields the free enzyme, which was supposed to be very unstable and rapidly denatured. However, one objection against this mechanism is the fact that sulfite is a more potent inhibitor than cyanide³, although it is a less active sulfur acceptor in rhodanese catalyzed reactions⁸.

It has now been observed that the inhibition of rhodanese with sulfite or cyanide required the presence of oxygen (Table 1) and that rhodanese, inhibited by sulfite or

Table 1. Effect of oxygen on sulfite and cyanide inhibition of rhodanese. Rhodanese (partially purified) was incubated with the inhibitor in Warburg flasks containing air or purified nitrogen as indicated. Inhibitor concentration was 0.01 M in all experiments, pH was 7.0 in case of sulfite and 7.4 in case of cyanide, time of incubation was 10 min in case of sulfite and 30 min in case of cyanide. Controls were run in nitrogen with omission of the inhibitor. Rhodanese activity was determined as in Ref. ⁶.

Inhibitor	Gas phase	Activity % of control
Sulfite	Air	0.5
"	Nitrogen	100
Cyanide	Air	4.3
"	Nitrogen	88.7

cyanide, could be reactivated by treatment with sulfhydryl compounds such as cysteamine, mercaptoethanol, or thioglycolate. Dialysis against phosphate buffer or sodium acetate gave no reactivation. If the enzyme was denatured by incubation with 8 M urea, neither dialysis against buffer nor treatment with sulfhydryl compounds had any reactivating effect. Thus the sulfhydryl compounds could not reactivate urea-denatured rhodanese, and their reactivating effect on sulfite- or cyanide-inhibited rhodanese must apparently be explained by another mechanism. Experiments with ³⁵S-labelled sulfite and crystalline rhodanese (Table 2) furthermore showed that the inhibitor became bound to the enzyme during the inhibition and was liberated again from the inhibited enzyme when the latter was reactivated by cysteamine. The rhodanese preparation used in these experiments was 3 times crystallized (specific activity 252 RU/mg) and contained 1.3 atoms of labile sulfur per molecule enzyme. The labile sulfur was determined by treating the enzyme with an excess of cyanide and colorimetric determination⁹ of the thiocyanate formed after the remaining cyanide had been removed by aeration from the acidified sample. The number of labile sulfur atoms per molecule rhodanese found for this preparation agreed with the number of sulfite molecules bound to one molecule of rhodanese during inhibition (Table 2). However, Westley and coworkers^{5,10} reported 1.5–1.9 atoms per molecule. When crystalline rhodanese was oxidized with performic acid¹¹ and cysteic acid determined with an automatic amino