Theoret. chim. Acta (Berl.) 12, 104—116 (1968)

Vibrational Analysis of Free Nine-Atomic and Bound Five-Atomic Tetrahedral Molecules

WAHBY WADIA*

Theoretical Physics Department, Atomic Energy Establishment, Cairo, Egypt, UAR

Received July 1, 1968

A theoretical investigation of the vibrational motion of a free nine-atomic tetrahedral molecule is given using Wilson's ***FG***-matrix method. By going to the limit of infinite mass of the outermost atoms, the vibrational frequences of a bound five-atomic tetrahedral molecule are obtained. This limiting case is also alternatively treated by the explicit consideration of the hindered translational and rotational motions. Such a model would probably approximate the state of affairs for amorphous substances with a tetrahedral basic unit.

Die Schwingungen eines freien, neunatomigen, tetraedrischen Moleküls werden analysiert. Indem man die Massen der äußersten Atome unendlich werden läßt, erhält man die Schwingungsfrequenzen eines gebundenen, fünfatomigen tetraedrischen Moleküls. Dieser Fall wurde auch direkt unter Berücksichtigung der Behinderung der Bewegungen behandelt. Dieses Modell könnte zur Beschreibung amorpher Substanzen aus tetraedrischen Grundeinheiten dienen.

Etude théorique du mouvement vibratoire d'une molécule libre tétraédrique à neuf atomes au moyen de la méthode de la matrice ***FG*** de Wilson. En passant à la limite de masse infinie des atomes périphériques, les fréquences vibrationnelles d'une molécule liée tétraédrique à cinq atomes sont obtenues. Ce cas limite est aussi traité par la considération explicité des mouvements de rotation et de translation non libres. Un tel modèle constitue probablement une approximation pour les substances amorphes à unité de base tétraédrique.

1. Introduction

The development of the theory of molecular vibrations based on group theory for symmetry considerations has been of great help in the understanding of the resulting spectra [1].

In this work, the vibrational motion of a free nine-atomic tetrahedral molecule AB_4C_4 is first considered using the ***FG***-matrix method [2] based on a previous work by Wilson [3]. A number of complexes of such tetrahedral symmetry are formed by metal cations with ligands [4] as CO, OH, NO and CN. In fact, the vibrational analysis of such a molecule has been previously considered by Crawford and Cross [5] using an approximate potential function and the results have been found to account satisfactorily for the infra-red and Raman spectra of nickelcarbonyl [6]. The analysis is here reconsidered assuming the most general harmonic potential function and using a complete set of internal coordinates [7].

By going to the limit of infinite mass of the outermost atoms C we then obtain the normal vibrations and frequencies of a five-atomic tetrahedral structure which is bound to four fixed "walls". Such a model would approximate the state of affairs of substances in a condensed phase, in particular, amorphous substances and with a tetrahedral basic unit which is no free but linked to the rest of the

* Present address: International Centre for Theoretical Physics, Trieste, Italy.

structure. In fact, this model has been considered using an alternative approach and it was found to account satisfactorily for the infra-red and Raman spectra of vitreous silica [8]. The model is, however, less adequate for periodic crystalline structures. Theoretical investigations of the translational and rotational motions of the molecules in molecular crystals have been attempted [9]. However, in these investigations the molecule was assumed to be rigid and the interaction between internal and collective vibrations is neglected.

The bound structure model is physically equivalent to the model in which, in addition to the internal vibrations, the translational and rotational motions are hindered by appropriate restoring forces. The latter is a general useful approach and it would be interesting to find out explicitly its relation to the alternative bound structure treatment. This investigation has been carried out in the case under consideration. Two forms of the potential energy, one describing a hindered tetrahedron and the other describing a bound one, have been considered. The relations between the "apparent" and "actual" force constants of the two forms, respectively, are then deduced.

2. Free Nine-Atomic Tetrahedral Molecule

2.1. Internal Coordinates and Symmetry Species

The genuine vibrations of a free nine-atomic tetrahedral molecule AB_4C_4, as shown in Fig. 1, can be described by $3N-6=21$ independent internal coordinates. Using the character table of the T_d-group representations, the species (symmetry types) of these vibrations are found to be

$$\Gamma = 2A_1 + 2E + F_1 + 4F_2\,, \tag{1}$$

where A_1, E, F_1, F_2 denote irreducible representations of the T_d-group. The four F_2-type frequencies are both infra-red and Raman active, the F_1-type frequency

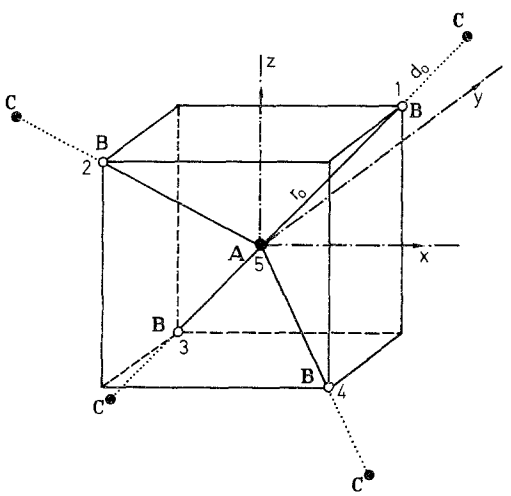

Fig. 1. Tetrahedral nine-atomic molecules AB_4C_4

is both infra-red and Raman inactive, while the two A_1-type and the two E-type frequencies are only Raman active. The A_1-type frequencies should be completely polarized [1, 2].

The following four equivalent sets of internal coordinates are chosen to describe the vibrational motion [7].

r_i $(i=1-4)$ the four A–B bond stretchings. They contain the symmetry species A_1, F_2.

d_i $(i=1-4)$ the four B–C bond stretchings. They contain the symmetry species A_1, F_2.

α_{ij} $(i=1-4, i\neq j, \alpha_{ij}=\alpha_{ji})$ the six BAB valence angle increments. They contain the symmetry species A_1, E, F_2.

β_{ij} $(i=1-4,\ i\neq j,\ \beta_{ij}\neq\beta_{ji})$ the twelve angles between each two bonds connected to atom i and in the plane of atoms i and j. The angle is considered positive when it lies on the side of atom j. They contain the symmetry species $A_1, E, F_1, 2F_2$.

There is a total of twenty-six coordinates which yield the representation

$$\Gamma' = 4A_1 + 2E + F_1 + 5F_2 . \tag{2}$$

Thus we have five redundancies of species $2A_1$, F_2. The redundancy conditions can be obtained from the forms of the $\boldsymbol{G}$-matrices as we shall see below.

2.2. *Potential and Kinetic Energy Expressions*

In terms of the above-introduced set of internal coordinates and taking into consideration the symmetry properties of the molecule, the most general potential energy in the harmonic approximation would be given by the expression

$$\begin{aligned}
2\mathscr{V} = {} & C_r(r_1^2+\cdots+r_4^2)+2C_{rr}(r_1r_2+\cdots+r_3r_4)+C_d(d_1^2+\cdots+d_4^2)\\
& +2C_{dd}(d_1d_2+\cdots+d_3d_4)+r_0^2C_\alpha(\alpha_{12}^2+\cdots+\alpha_{34}^2)\\
& +2r_0^2C_{\alpha\alpha}(\alpha_{12}\alpha_{34}+\cdots+\alpha_{14}\alpha_{23})+2r_0^2C'_{\alpha\alpha}(\alpha_{12}\alpha_{13}+\cdots+\alpha_{24}\alpha_{34})\\
& +r_0^2C_\beta(\beta_{12}^2+\cdots+\beta_{43}^2)+2r_0^2C_{\beta\beta}(\beta_{12}\beta_{34}+\cdots+\beta_{21}\beta_{43})\\
& +2r_0^2C'_{\beta\beta}(\beta_{12}\beta_{21}+\cdots+\beta_{34}\beta_{43})+2r_0^2C''_{\beta\beta}(\beta_{12}\beta_{23}+\cdots+\beta_{43}\beta_{32})\\
& +2r_0^2C'''_{\beta\beta}(\beta_{12}\beta_{13}+\cdots+\beta_{42}\beta_{43})+2r_0^2C''''_{\beta\beta}(\beta_{12}\beta_{32}+\cdots+\beta_{23}\beta_{43})\\
& +2C_{rd}(r_1d_1+\cdots+r_4d_4)+2C'_{rd}(r_1d_2+\cdots+r_4d_3)\\
& +2r_0C_{r\alpha}(r_1\alpha_{12}+\cdots+r_4\alpha_{34})+2r_0C'_{r\alpha}(r_1\alpha_{23}+\cdots+r_4\alpha_{23})\\
& +2r_0C_{r\beta}(r_1\beta_{21}+\cdots+r_4\beta_{34})+2r_0C'_{r\beta}(r_1\beta_{12}+\cdots+r_4\beta_{43})\\
& +2r_0C''_{r\beta}(r_1\beta_{23}+\cdots+r_4\beta_{32})+2r_0C_{d\alpha}(d_1\alpha_{12}+\cdots+d_4\alpha_{34})\\
& +2r_0C'_{d\alpha}(d_1\alpha_{23}+\cdots+d_4\alpha_{23})+2r_0C_{d\beta}(d_1\beta_{21}+\cdots+d_4\beta_{34})\\
& +2r_0C'_{d\beta}(d_1\beta_{12}+\cdots+d_4\beta_{43})+2r_0C''_{d\beta}(d_1\beta_{23}+\cdots+d_4\beta_{32})\\
& +2r_0^2C_{\alpha\beta}(\alpha_{12}\beta_{12}+\cdots+\alpha_{34}\beta_{34})+2r_0^2C'_{\alpha\beta}(\alpha_{12}\beta_{31}+\cdots+\alpha_{34}\beta_{23})\\
& +2r_0^2C''_{\alpha\beta}(\alpha_{12}\beta_{13}+\cdots+\alpha_{34}\beta_{32})+2r_0^2C'''_{\alpha\beta}(\alpha_{12}\beta_{34}+\cdots+\alpha_{34}\beta_{21}),
\end{aligned} \tag{3}$$

where the C's are the force constants and r_0 is the equilibrium interatomic distances A–B. Expression (3) has twenty-nine constants, as it should be, since $\Sigma n_\gamma(n_\gamma+1)/2 = 29$, where n_γ are given by the coefficients on the right-hand side of Eq. (2). However, it follows from Eq. (1) that $\Sigma n_\gamma(n_\gamma+1)/2 = 17$; there can be, therefore,

only seventeen independent constants. Hence there are twelve redundant constants. As we shall see, the excessive force constants can be easily visualized and treated after the introduction of the symmetry coordinates.

In terms of the internal coordinates the kinetic energy has a similar form as that of the potential energy expression (3). The matrix-elements of the $\boldsymbol{K}$-matrix of the kinetic energy, which are functions of the atomic masses and the geometrical constants of the molecule in its equilibrium position, remain to be evaluated. Devices and formulae have been developed for the evaluation of $\boldsymbol{K}$-matrix elements corresponding to various combinations of internal coordinates [2]. Applying these rules the k-constants can be readily evaluated and are found to be

$$k_r = \mu_c + \mu_1, \quad k_{rr} = -\frac{1}{3}\mu_c, \quad k_d = \mu_1 + \mu_2, \quad k_{dd} = 0,$$

$$k_\alpha = 2\mu_1 + \frac{8}{3}\mu_c, \quad k_{\alpha\alpha} = -\frac{8}{3}\mu_c, \quad k'_{\alpha\alpha} = -\frac{1}{2}\mu_1,$$

$$k_\beta = \mu_c + (1+\gamma)^2\mu_1 + \gamma^2\mu_2, \quad k_{\beta\beta} = -\frac{2}{3}\mu_c, \quad k'_{\beta\beta} = \frac{1}{3}\mu_c,$$

$$k''_{\beta\beta} = -\frac{1}{6}\mu_c, \quad k'''_{\beta\beta} = -\frac{1}{2}\{\mu_c + (1+\gamma)^2\mu_1 + \gamma^2\mu_2\}, \quad k''''_{\beta\beta} = \frac{5}{6}\mu_c,$$

$$k_{rd} = -\mu_1, \quad k'_{rd} = 0, \quad k_{r\alpha} = -\frac{2\sqrt{2}}{3}\mu_c, \quad k'_{r\alpha} = \frac{2\sqrt{2}}{3}\mu_c,$$

$$k_{r\beta} = -\frac{2\sqrt{2}}{3}\mu_c, \quad k'_{r\beta} = 0, \quad k''_{r\beta} = \frac{\sqrt{2}}{3}\mu_c, \quad k_{d\alpha} = k'_{d\alpha} = 0,$$

$$k_{d\beta} = k'_{d\beta} = k''_{d\beta} = 0, \quad k_{\alpha\beta} = (1+\gamma)\mu_1 + \frac{4}{3}\mu_c, \quad k'_{\alpha\beta} = \frac{2}{3}\mu'_c,$$

$$k''_{\alpha\beta} = -\frac{2}{3}\mu_c - \frac{1}{2}(1+\gamma)\mu_1, \quad k'''_{\alpha\beta} = -\frac{4}{3}\mu_c, \tag{4}$$

where

$$\mu_c = \frac{1}{m_c}, \quad \mu_1 = \frac{1}{m_1}, \quad \mu_2 = \frac{1}{m_2}, \tag{5}$$

are the reciprocals of the masses of the atoms A, B, C, respectively, and

$$\gamma = \frac{r_0}{d_0}, \tag{6}$$

where r_0 and d_0 are the equilibrium interatomic distances A–B and B–C respectively.

*2.3. Symmetry Coordinates-**F**- and **G**-Matrices*

In order to attain maximum factorization of the secular equation, it is necessary to construct properly oriented symmetry coordinates [2]. The $\boldsymbol{F}$- and $\boldsymbol{G}$-matrices of the potential and kinetic energy expressions, respectively, have then to be calculated in terms of the new symmetry coordinates. These can be readily

obtained by the methods developed for this purpose [2]. According to Eq. (2), the secular equation originally of degree twenty-six reduces to a quartic factor determining the vibrations of the non-degenerate species A_1, two identical quadratic factors determining the vibrations of the doubly degenerate species E, three identical single factors determining the vibration of thr triply degenerate species F_1 and three identical quantic factors determining the vibrations of the triply degenerate species F_2. As indicated in Section 2.1, species A_1, E, F_1 each occur at most once for every equivalent set. In this case, a representative of each of these species can be constructed in a straightforward manner [2]. The properly oriented generating coordinates for the various equivalent sets are chosen to be r_1+r_2, d_1+d_2, α_{12}, $\beta_{12}+\beta_{21}$ which are invariant with respect to a subgroup C_{2v} of T_d.

The equivalent set of the β-coordinates contributes two F_2-species and the construction of the symmetry coordinates of type F_2 requires, therefore, special consideration. In such cases, where an equivalent set of coordinates contributes more than one species of a certain type, it has been shown by Wilson *et al.* [2] that it is always possible by the help of a properly chosen subgroup K of the symmetry group to reorganize the original set of internal coordinates into non-mixing subsets. Each subset contains a certain species at most once. The usual methods and rules could then be applied to each subset separately. In our case the subgroup C_{2v} is found suitable to be K. The twelve β-coordinates can, then, be reorganized into two non-mixing sets each containing six equivalent members, namely

$$K_1=\frac{1}{\sqrt{2}}(\beta_{12}+\beta_{21}),\quad K_2=\frac{1}{\sqrt{2}}(\beta_{13}+\beta_{31}),\quad K_3=\frac{1}{\sqrt{2}}(\beta_{14}+\beta_{41})$$

$$K_4=\frac{1}{\sqrt{2}}(\beta_{23}+\beta_{32}),\quad K_4=\frac{1}{\sqrt{2}}(\beta_{24}+\beta_{42}),\quad K_6=\frac{1}{\sqrt{2}}(\beta_{34}+\beta_{43}),\qquad (7a)$$

and

$$K'_1=\frac{1}{\sqrt{2}}(\beta_{12}-\beta_{21}),\quad K'_2=\frac{1}{\sqrt{2}}(\beta_{13}-\beta_{31}),\quad K'_3=\frac{1}{\sqrt{2}}(\beta_{14}-\beta_{41}),$$

$$K'_4=\frac{1}{\sqrt{2}}(\beta_{23}-\beta_{32}),\quad K'_5=\frac{1}{\sqrt{2}}(\beta_{24}-\beta_{42}),\quad K'_6=\frac{1}{\sqrt{2}}(\beta_{34}-\beta_{43}).\qquad (7b)$$

The problems of redundancy can then be readily treated. It has been shown by Wilson *et al.* [2] that if a linear combination of coordinates vanishes, so does the same linear combination of the corresponding $\boldsymbol{G}$-matrix elements in any row or column. The redundancy conditions can be, therefore, directly deduced from the forms of the $\boldsymbol{G}$-matrices and are found to be

$$(\alpha_{12}+\alpha_{13}+\alpha_{14}+\alpha_{23}+\alpha_{24}+\alpha_{34})=0,\qquad (8a)$$

$$(\beta_{12}+\beta_{13}+\beta_{14}+\beta_{21}+\beta_{23}+\beta_{24}+\beta_{31}+\beta_{32}+\beta_{34}+\beta_{41}+\beta_{42}+\beta_{43})=0\qquad (8b)$$

of type A_1, and

$$(\beta_{12}+\beta_{13}+\beta_{14}+\beta_{21}+\beta_{23}+\beta_{24}-\beta_{31}-\beta_{32}-\beta_{34}-\beta_{41}-\beta_{42}-\beta_{43})=0\qquad (8c)$$

of type F_2 as stated before. The redundancy conditions given by Eqs. (8) together with two conditions similar to Eq. (8c) and corresponding to the other two symmetry coordinates of species F_2 amount to the rather obvious redundant conditions

$$\sum_{j \neq i} \beta_{ij} = 0, \qquad i = 1, 2, 3, 4 . \tag{9}$$

Next we consider the redundant force constants. For this purpose the potential energy and the redundant relations (8) are expressed in terms of the symmetry coordinates. The redundant coordinates are then eliminated from the potential energy expression. It is then found that the force constants appear only in seventeen independent combinations. In particular, it is found that the sets of constants $(C_\alpha, C_{\alpha\alpha}, C'_{\alpha\alpha})$, $(C_\beta, C_{\beta\beta}, C'_{\beta\beta}, C''_{\beta\beta}, C'''_{\beta\beta}, C''''_{\beta\beta})$, $(C_{r\alpha}, C'_{r\alpha})$, $(C_{r\beta}, C'_{r\beta}, C''_{r\beta})$, $(C_{d\alpha}, C'_{d\alpha})$, $(C_{d\beta}, C'_{d\beta}, C''_{d\beta})$. $(C_{\alpha\beta}, C'_{\alpha\beta}, C''_{\alpha\beta}, C'''_{\alpha\beta})$ appear only in 2, 3, 1, 1, 1, 1, 2 combinations, respectively. Without loss of generalization, it is therefore perfectly allowable to put, respectively, 1, 3, 1, 2, 1, 2, 2 (twelve in total) force constants, or linear combinations from the previous sets equal to zeros. However, one has to be sure that the remaining combinations are linear independent. We arbitrarily choose

$$C'_{\alpha\alpha} = C''_{\beta\beta} = C'''_{\beta\beta} = C''''_{\beta\beta} = C'_{r\alpha} = C'_{r\beta} = C''_{r\beta} = C'_{d\alpha} = C'_{d\beta} = C''_{d\beta} = C''_{\alpha\beta} = C'''_{\alpha\beta} = 0 . \tag{10}$$

In terms of the remaining seventeen force constants, the nine (partly degenerate) normal frequencies of a nine-atomic tetrahedral molecule are given by the roots of the secular equations

$$|\boldsymbol{G}^{(\gamma)}\boldsymbol{F}^{(\gamma)} - \lambda \boldsymbol{E}| = 0 , \tag{11}$$

where the $\boldsymbol{F}^{(\gamma)}$ and $\boldsymbol{G}^{(\gamma)}$ matrices together with the corresponding symmetry coordinate (one component for each degenerate species) have the following forms:

A_1-species (λ_1, λ'_1)

$$S_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4),$$

$$S'_1 = \frac{1}{2}(d_1 + d_2 + d_3 + d_4); \tag{12a}$$

$$\boldsymbol{G} = \begin{bmatrix} \mu_1 & -\mu_1 \\ & \mu_1 + \mu_2 \end{bmatrix}, \tag{12b}$$

$$\boldsymbol{F} = \begin{bmatrix} C_r + 3C_{rr} & C_{rd} + 3C'_{rd} \\ & C_d + 3C_{dd} \end{bmatrix}. \tag{12c}$$

E-species (λ_2, λ'_2)

$$S_2 = \frac{1}{\sqrt{12}}(2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34}),$$

$$S_2^1 = \frac{1}{\sqrt{24}}(2\beta_{12} - \beta_{13} - \beta_{14} + 2\beta_{21} - \beta_{23} - \beta_{24} - \beta_{31} - \beta_{32} + 2\beta_{34} - \beta_{41} - \beta_{42} + 2\beta_{43}); \tag{13a}$$

$$\boldsymbol{G}=\begin{bmatrix} 3\mu_1 & \frac{3\sqrt{2}}{2}(1+\gamma)\mu_1 \\ & \frac{3}{2}(1+\gamma)^2\mu_1+\frac{3}{2}\gamma^2\mu_2 \end{bmatrix}, \tag{13b}$$

$$\boldsymbol{F}=\begin{bmatrix} C_\alpha+C_{\alpha\alpha} & \sqrt{2}(C_{\alpha\beta}-C'_{\alpha\beta}) \\ & C_\beta+2C_{\beta\beta}+C'_{\beta\beta} \end{bmatrix}. \tag{13c}$$

F_1-species (λ_3)

$$S_3=\frac{1}{4}(2\beta_{12}-\beta_{13}-\beta_{14}-2\beta_{21}+\beta_{23}+\beta_{24}+\beta_{31}-\beta_{32}+\beta_{41}-\beta_{42}); \tag{14a}$$

$$\boldsymbol{G}=\frac{3}{2}(1+\gamma)^2\mu_1+\frac{3}{2}\gamma^2\mu_2, \tag{14b}$$

$$\boldsymbol{F}=C_\beta-C'_{\beta\beta}. \tag{14c}$$

F_2-species ($\lambda_4, \lambda'_4, \lambda''_4, \lambda'''_4$)

$$\begin{aligned} S_4&=\frac{1}{2}(r_1+r_2-r_3-r_4), \\ S'_4&=\frac{1}{2}(d_1+d_2-d_3-d_4), \\ S''_4&=\frac{1}{\sqrt{2}}(\alpha_{12}-\alpha_{34}), \\ S'''_4&=\frac{1}{2}(\beta_{12}+\beta_{21}-\beta_{34}-\beta_{43}), \end{aligned} \tag{15a}$$

$$\boldsymbol{G}=\begin{bmatrix} \mu_1+\frac{4}{3}\mu_c & -\mu_1 & -\frac{8}{3}\mu_c & \frac{-4\sqrt{2}}{3}\mu_c \\ & \mu_1+\mu_2 & 0 & 0 \\ & & 2\mu_1+\frac{16}{3}\mu_c & \sqrt{2}(1+\gamma)\mu_1+\frac{8\sqrt{2}}{3}\mu_c \\ & & & (1+\gamma)^2\mu_1+\frac{8}{3}\mu_c+\gamma^2\mu_2 \end{bmatrix}, \tag{15b}$$

$$\boldsymbol{F}=\begin{bmatrix} C_r-C_{rr} & C_{rd}-C'_{rd} & \sqrt{2}C_{r\alpha} & 2C_{r\beta} \\ & C_d-C_{dd} & \sqrt{2}C_{d\alpha} & 2C_{d\beta} \\ & & C_\alpha-C_{\alpha\alpha} & \sqrt{2}(C_{\alpha\beta}+C'_{\alpha\beta}) \\ & & & \frac{3}{2}C_\beta-2C_{\beta\beta}+\frac{1}{2}C'_{\beta\beta} \end{bmatrix}. \tag{15c}$$

3. Bound Five-Atomic Tetrahedral Molecule

By going to the limit of an infinite mass of the outermost atoms C($m_2=\infty$, $\mu_2=0$), we obtain the case of a five-atomic tetrahedral structure AB_4 linked to

"fixed walls" placed at the A–B bond extensions. From the character table we find that for structure of symmetry T_d the translations and rotations are of species F_2 and F_1, respectively. For a bound structure, small translations and rotations are opposed by restoring forces which render them as genuine vibrations. A bound five-atomic tetrahedral structure has, therefore, a total of normal vibrations of the following species:

$$\Gamma'' = A_1 + E + F_1 + 3F_2 . \tag{16}$$

Comparing Eq. (16) with Eq. (1) we find that three frequencies (degeneracy not counted) of the free nine-atomic molecule AB_4C_4 of types A_1, E, F_2 will have zero values in the limit $\mu_2 = 0$.

That some frequencies go over to zero in the limit $m_2 = \infty$ implies also the appearance of additional redundances. This is of course physically clear since imposed constraints give rise to mathematical relation between the coordinates. The additional redundancies can be directly obtained by puting $\mu_2 = 0$ in the $\boldsymbol{G}$-matrices given by Eqs. (12b) to (15b) and are found to be

$$S_1 + S_1' = 0 , \tag{17a}$$

$$\frac{\sqrt{2}}{2}(1+\gamma)S_2 - S_2' = 0 , \tag{17b}$$

$$S_4 + S_4' + \frac{1+\gamma}{2\gamma} S_4'' - \frac{\sqrt{2}}{2\gamma} S_4''' = 0 . \tag{17c}$$

The redundancy can be treated in an analogous way as indicated before. When the symmetry coordinates are eliminated from the potential energy function by means of Eqs. (17), it is found that 17 constants appearing in the $\boldsymbol{F}$-matrices of Eqs. (12c) to (15c) occur only in 9 independent combinations, as Eq. (16) also implies. We arbitrarily put the following 8 constants equal to zero:

$$C_{rd}' = C_{dd} = C_{\alpha\beta} = C_{\alpha\beta}' = C_{\beta\beta} = C_{\beta\beta}' = C_{r\beta} = C_{d\beta} = 0 . \tag{18}$$

Hence, we get for the bound AB_4 tetrahedron the following $\boldsymbol{F}$ and $\boldsymbol{G}$-matrices as derived from those given by Eqs. (12)–(15) and in terms of the remaining nine constants

$$\boldsymbol{C} = (C_r, C_d, C_\alpha, C_\beta, C_{rr}, C_{rd}, C_{r\alpha}, C_{d\alpha}, C_{\alpha\alpha}) . \tag{19}$$

A_1-species (λ_1)

$$\boldsymbol{G} = \mu_1 , \quad \boldsymbol{F} = C_r + C_d + 3C_{rr} - 2C_{rd} . \tag{20}$$

E-species (λ_2)

$$\boldsymbol{G} = 3\mu_1 , \quad \boldsymbol{F} = C_\alpha + C_{\alpha\alpha} + \frac{(1+\gamma)^2}{2} C_\beta . \tag{21}$$

F_1-species (λ_3)

$$\boldsymbol{G} = \frac{3}{2}(1+\gamma)^2 \mu_1 , \quad \boldsymbol{F} = C_\beta . \tag{22}$$

F_2-*species* ($\lambda_4, \lambda_4', \lambda_4''$)

$$\boldsymbol{G}=\begin{bmatrix} \mu_1+\frac{4}{3}\mu_c & -\mu_1 & -\frac{8}{3}\mu_c \\ -\mu_1 & \mu_1 & 0 \\ -\frac{8}{3}\mu_c & 0 & 2\mu_1+\frac{16}{3}\mu_c \end{bmatrix}, \tag{23}$$

$$\boldsymbol{F}=\begin{bmatrix} C_r-C_{rr}+3\gamma^2C_\beta & C_{rd}+3\gamma^2C_\beta & \sqrt{2}C_{r\alpha}+\frac{3}{2}\gamma(1+\gamma)C_\beta \\ C_{rd}+3\gamma^2C_\beta & C_d+3\gamma^2C_\beta & \sqrt{2}C_{d\alpha}+\frac{3}{2}\gamma(1+\gamma)C_\beta \\ \sqrt{2}C_{r\alpha}+\frac{3}{2}\gamma(1+\gamma)C_\beta & \sqrt{2}C_{d\alpha}+\frac{3}{2}\gamma(1+\gamma)C_\beta & C_\alpha-C_{\alpha\alpha}+\frac{3}{4}(1+\gamma)^2C_\beta \end{bmatrix}.$$

If the interaction constants are neglected, the normal frequencies will have a relatively simple dependence on the remaining four constants C_r, C_d, C_α, C_β. The behaviour of the normal frequencies given by Eqs. (12)–(15) as the mass m_2 of outermost atoms C changes from 1 a.m.u. to infinity for selected values of the force constants and atomic masses is illustrated in Fig. 2.

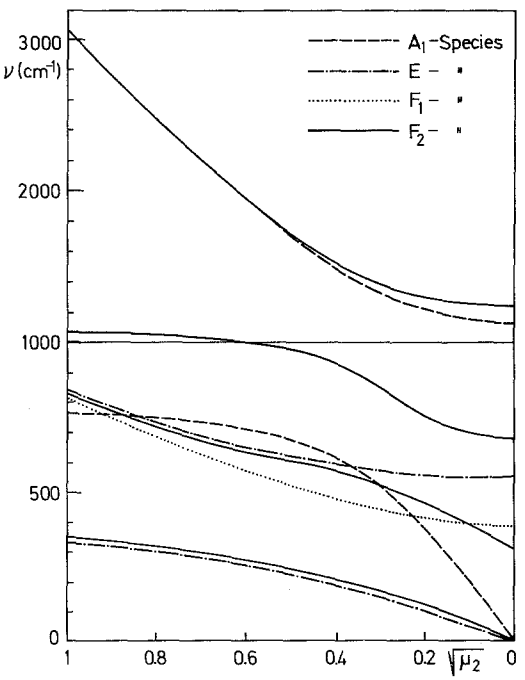

Fig. 2. Normal vibrational frequencies of a tetrahedral nine-atomic molecule AB_4C_4 as a function of the mass $m_2 = 1/\mu_2$ of C (see Eqs. (12)–(15)) for the set of values: $C_r = C_d = 5.0$, $C_\alpha = 0.4$, $C_\beta = 0.2$ for the force constants; $\mu_c = 0.036$, $\mu_1 = 0.075$ for the reciprocal of the masses of A and B; respectively; $\gamma = 1$ for the ratio of the atomic distances. Masses are in atomic mass units and force constants are in units of 10^5 dynes cm^{-1}. Interaction constants are neglected. Notice the change in the scale on the ordinate

By putting $C_d = C_\beta = C_{rd} = C_{d\alpha} = 0$ in Eqs. (20)–(23) we get, as a special case, the genuine vibrations of a free five-atomic tetrahedral molecule in the most general simple harmonic potential which would contain five force constants [10]. We find

$$\lambda_1 = \mu_1 (C_r + 3 C_{rr}), \tag{24}$$

$$\lambda_2 = 3 \mu_1 (C_\alpha + C_{\alpha\alpha}), \tag{25}$$

$$\lambda_4 + \lambda_4' = \left(\mu_1 + \frac{4}{3}\mu_c\right)(C_r - C_{rr}) + 2\left(\mu_1 + \frac{8}{3}\mu_c\right)(C_\alpha - C_{\alpha\alpha}) - \frac{16\sqrt{2}}{3}\mu_c C_{r\alpha},$$

$$\lambda_4 \lambda_4' = 2\mu_1(\mu_1 + 4\mu_c)\{(C_r - C_{rr})(C_\alpha - C_{\alpha\alpha}) - 2C_{r\alpha}^2\}, \tag{26}$$

where λ_1 is of species A_1, λ_2 of species E and λ_4, λ_4' are of species F_2.

4. Hindered Five-Atomic Tetrahedral Molecules

The motion of the bound five-atomic tetrahedron previously discussed is physically equivalent to imposing restoring simple harmonic forces on its translational and rotational motions in addition to its internal vibrations. It would, therefore, be interesting to treat such a hindered motion explicitly and to compare the result with that of the previous treatment. For this purpose we introduce, in addition to the sets r_i and α_{ij} describing the internal motion, the coordinates $\boldsymbol{t} = (t_1, t_2, t_3)$ and $\boldsymbol{\delta} = (\delta_1, \delta_2, \delta_3)$ representing small translations and rotations, where the subscripts 1, 2, 3 stand for the x, y, and z components, respectively. In terms of cartesian displacements, they have the form

$$t_1 = \frac{1}{M}\{m_1(x_1 + x_2 + x_3 + x_4) + m_c x_5\}, \tag{27}$$

$$\delta_1 = \frac{\sqrt{3}}{8 r_0}\{(-y_1 - y_2 + y_3 + y_4) + (z_1 - z_2 + z_3 - z_4)\}, \tag{28}$$

with similar expressions for the other components, and where

$$M = 1/\mu = m_c + 4 m_1 \tag{29}$$

is the total mass of the molecule. From symmetry considerations the most general potential energy function in harmonic approximation is readily found to be

$$\begin{aligned} 2\mathscr{V} = {} & \bar{C}_r(r_1^2 + \cdots + r_4^2) + 2\bar{C}_{rr}(r_1 r_2 + \cdots + r_3 r_4) \\ & + r_0^2 \bar{C}_\alpha(\alpha_{12}^2 + \cdots + \alpha_{34}^2) + 2 r_0^2 \bar{C}_{\alpha\alpha}(\alpha_{12}\alpha_{34} + \cdots + \alpha_{14}\alpha_{23}) \\ & + \bar{C}_t(t_1^2 + t_2^2 + t_3^2) + r_0^2 \bar{C}_\delta(\delta_1^2 + \delta_2^2 + \delta_3^2) + 2 r_0 \bar{C}_{r\alpha}(r_1\alpha_{12} + \cdots + r_4\alpha_{34}) \\ & + 2\bar{C}_{rt}\{t_1(r_1 - r_2 - r_3 + r_4) + t_2(r_1 - r_2 + r_3 - r_4) + t_3(r_1 + r_2 - r_3 - r_4)\} \\ & + 2 r_0 \bar{C}_{t\alpha}\{t_1(\alpha_{14} - \alpha_{23}) + t_2(\alpha_{13} - \alpha_{24}) + t_3(\alpha_{12} - \alpha_{34})\}, \end{aligned} \tag{30}$$

where the force constants are designated by the bars to distinguish them from those appearing in Eq. (3). In Eq. (30) we have put the redundant constants $\bar{C}_{\alpha\alpha}' = \bar{C}_{r\alpha}' = 0$ as deduced from Eq. (10), so that the above expression of the potential energy contains only nine constants as it should be for a representation given by Eq. (16). The kinetic energy has an analogous expression to that of Eq. (30). The

kinetic energy constants $k_r, k_{rr}, k_\alpha, k_{\alpha\alpha}, k_{r\alpha}$ are again given by Eq. (4). The remaining four k-constants can be readily evaluated by a straightforward generalization of Wilson's method and are found to have the values

$$k_t = \mu, \quad k_\delta = \frac{3}{8}\mu_1, \quad k_{rt} = k_{t\alpha} = 0. \tag{31}$$

The following are the symmetry coordinates and the corresponding $\boldsymbol{F}$ and $\boldsymbol{G}$-matrices as can be easily verified (after the removal of the only A_1-redundancy).

A_1-species (λ_1)

$$\bar{S}_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4); \tag{32a}$$

$$\bar{\boldsymbol{G}} = \mu_1, \quad \bar{\boldsymbol{F}} = \bar{C}_r + 3\bar{C}_{rr}. \tag{32b}$$

E-species (λ_2)

$$\bar{S}_2 = \frac{1}{\sqrt{12}}(2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34}); \tag{33a}$$

$$\bar{\boldsymbol{G}} = 3\mu_1, \quad \bar{\boldsymbol{F}} = \bar{C}_\alpha + \bar{C}_{\alpha\alpha}. \tag{33b}$$

F_1-species (λ_3)

$$\bar{S}_3 = \delta_1; \tag{34a}$$

$$\bar{\boldsymbol{G}} = \frac{3}{8}\mu_1, \quad \bar{\boldsymbol{F}} = \bar{C}_\delta. \tag{34b}$$

F_2-species ($\lambda_4, \lambda_4', \lambda_4''$)

$$\bar{S}_4 = \frac{1}{2}(r_1 + r_2 - r_3 - r_4),$$

$$\bar{S}_4' = t_3,$$

$$\bar{S}_4'' = \frac{1}{\sqrt{2}}(\alpha_{12} - \alpha_{34}); \tag{35a}$$

$$\bar{\boldsymbol{G}} = \begin{bmatrix} \mu_1 + \frac{4}{3}\mu_c & 0 & -\frac{8}{3}\mu_c \\ 0 & \mu & 0 \\ -\frac{8}{3}\mu_c & 0 & 2\mu_1 + \frac{16}{3}\mu_c \end{bmatrix}, \quad \bar{\boldsymbol{F}} = \begin{bmatrix} \bar{C}_r - \bar{C}_{rr} & 2\bar{C}_{rt} & \sqrt{2}\bar{C}_{r\alpha} \\ 2\bar{C}_{rt} & \bar{C}_t & \sqrt{2}\bar{C}_{t\alpha} \\ \sqrt{2}\bar{C}_{r\alpha} & \sqrt{2}\bar{C}_{t\alpha} & \bar{C}_\alpha - \bar{C}_{\alpha\alpha} \end{bmatrix}. \tag{35b}$$

The relations between the $\bar{C}$-constants and the C-constants can be obtained by comparing the $\boldsymbol{F} - \boldsymbol{G}$-matrices in both cases as given by Eqs. (20)–(23) and Eqs. (32)–(35). However, in the case of F_2-species $\bar{G} \neq G$ and it is therefore not adequate to put $\bar{\boldsymbol{G}}\bar{\boldsymbol{F}} = \boldsymbol{G}\boldsymbol{F}$. Such an equality would lead to the relation $\boldsymbol{F} = \bar{\boldsymbol{G}}^{-1}\boldsymbol{G}\boldsymbol{F}$ which cannot be valid since its left-hand side is a symmetrical matrix while the right-hand side is not. In fact the corresponding matrices are connected together by an equivalent transformation. For, suppose the two sets of coordinates

$S=(S_4, S_4', S_4'')$ and $\bar{S}=(\bar{S}_4, \bar{S}_4', \bar{S}_4'')$ as given by Eqs. (15a) and Eqs. (35a), respectively, are connected together, in the matrix notation, by the linear relation

$$\boldsymbol{S}=\boldsymbol{V}\bar{\boldsymbol{S}}, \quad \bar{\boldsymbol{S}}=\boldsymbol{U}\boldsymbol{S}; \quad \boldsymbol{U}\boldsymbol{V}=\boldsymbol{E}. \tag{36}$$

Now, the form of the parts of the potential and kinetic energies corresponding to the F_2-species are

$$2\mathscr{V}=\boldsymbol{S}^+\boldsymbol{F}\boldsymbol{S}=\bar{\boldsymbol{S}}^+\bar{\boldsymbol{F}}\bar{\boldsymbol{S}}, \tag{37a}$$

$$2\mathscr{T}=\dot{\boldsymbol{S}}^+\boldsymbol{G}^{-1}\dot{\boldsymbol{S}}=\dot{\bar{\boldsymbol{S}}}^+\boldsymbol{G}^{-1}\dot{\bar{\boldsymbol{S}}}. \tag{37b}$$

From Eqs. (36) and (37) we find

$$\bar{\boldsymbol{F}}=\boldsymbol{V}^+\boldsymbol{F}\boldsymbol{V}=(\boldsymbol{U}^+)^{-1}\boldsymbol{F}\boldsymbol{U}^{-1}, \tag{38a}$$

$$\bar{\boldsymbol{G}}=\boldsymbol{U}\boldsymbol{G}\boldsymbol{U}^+=\boldsymbol{V}^{-1}\boldsymbol{G}(\boldsymbol{V}^+)^{-1}. \tag{38b}$$

Hence,

$$\bar{\boldsymbol{G}}\bar{\boldsymbol{F}}=\boldsymbol{U}\boldsymbol{G}\boldsymbol{F}\boldsymbol{U}^{-1}, \tag{39}$$

which shows that $\bar{\boldsymbol{G}}\bar{\boldsymbol{F}}$ and $\boldsymbol{G}\boldsymbol{F}$ have the same normal frequencies. The matrix $\boldsymbol{U}$ and its reciprocal $\boldsymbol{V}$ can be readily found from Eq. (38b) and the forms of $\boldsymbol{G}$ and $\bar{\boldsymbol{G}}$ as given by Eqs. (23) and (35b), respectively. We find

$$\boldsymbol{U}=\begin{bmatrix} 1 & 0 & 0 \\ -\dfrac{-8m_1+3m_c}{2\sqrt{3}M} & \dfrac{-\sqrt{3}}{2} & \dfrac{-2m_1}{\sqrt{3}M} \\ 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{V}=\begin{bmatrix} 1 & 0 & 0 \\ -\dfrac{8m_1+3m_c}{3M} & \dfrac{-2}{\sqrt{3}} & -\dfrac{4m_1}{3M} \\ 0 & 0 & 1 \end{bmatrix}. \tag{40}$$

Comparing Eqs. (20)–(23) with Eqs. (32b)–(35b) and making use of Eqs. (38)–(40) we obtain the relations between the C-constants in Eq. (19) describing a bound five-atomic tetrahedral structure and the $\bar{C}$-constants appearing in Eq. (30) and describing a hindered one. One gets

$$\bar{C}_r=C_r+\left(1-2\varrho+\frac{4}{3}\varrho^2\right)C_d-2(1-\varrho)C_{rd}+4\varrho^2\gamma^2C_\beta$$

$$\bar{C}_{rr}=C_{rr}+\frac{2}{3}\varrho\left(1-\frac{2}{3}\varrho\right)C_d-\frac{2}{3}\varrho C_{rd}-\frac{4}{3}\varrho^2\gamma^2C_\beta$$

$$\bar{C}_\alpha=C_\alpha+\frac{8}{9}\varrho^2C_d-\frac{4\sqrt{2}}{3}\varrho C_{d\alpha}+\left\{\frac{8}{3}\varrho^2\gamma^2-2\varrho\gamma(1+\gamma)+\frac{5}{8}(1+\gamma)^2\right\}C_\beta$$

$$\bar{C}_{\alpha\alpha}=C_{\alpha\alpha}-\frac{8}{9}\varrho^2C_d+\frac{4\sqrt{2}}{3}\varrho C_{d\alpha}-\left\{\frac{8}{3}\varrho^2\gamma^2-2\varrho\gamma(1+\gamma)+\frac{1}{8}(1+\gamma)^2\right\}C_\beta$$

$$\bar{C}_{r\alpha}=C_{r\alpha}-\frac{2\sqrt{2}}{3}\varrho C_{rd}+\frac{2\sqrt{2}}{3}\varrho\left(1-\frac{4}{3}\varrho\right)C_d-\left(1-\frac{4}{3}\varrho\right)C_{d\alpha}$$
$$+\sqrt{2}\varrho\gamma\left\{1+\gamma-\frac{8}{3}\varrho\gamma\right\}C_\beta$$

$$\bar{C}_{rt} = -\frac{1}{\sqrt{3}} C_{rd} + \frac{1}{\sqrt{3}} \left(1 - \frac{4}{3}\varrho\right) C_d - \frac{4}{\sqrt{3}} \varrho\gamma^2 C_\beta ,$$

$$\bar{C}_{t\alpha} = -\frac{2}{\sqrt{3}} C_{d\alpha} + \frac{4\sqrt{2}}{3\sqrt{3}} \varrho C_d + \sqrt{6} \left\{\frac{4}{3}\varrho\gamma^2 - \frac{1}{2}\gamma(1+\gamma)\right\} C_\beta$$

$$\bar{C}_t = \frac{4}{3}(C_d + 3\gamma^2 C_\beta), \qquad \bar{C}_\delta = 4(1+\gamma)^2 C_\beta , \tag{41}$$

where

$$\varrho = \frac{m_1}{M} = \frac{\mu}{\mu_1} . \tag{42}$$

The inverse relations expressing the C-constants in terms of the $\bar{C}$-constants can be similarly obtained.

Acknowledgments. The author wishes to express his sincere thanks to Professor A. Bishay, Professor M. El-Nadi and Professor E. B. Wilson Jr., for their interest and encouragement.

References

1. Mattossi, F.: Gruppentheorie der Eigenschwingungen von Punktsystemen. Berlin-Göttingen-Heidelberg: Springer 1961.
   Nielsen, H. H.: Handbuch der Physik XXXVII 1, p. 173. Berlin-Göttingen-Heidelberg: Springer 1959.
   Herzberg, G.: Infra-red and Raman spectra of polyatomic molecules. New York: D. Van Norstrand 1945.
2. Wilson, Jr., E. B., J. C. Decius, and P. C. Cross: Molecular vibrations. New York: McGraw-Hill 1955.
3. — J. chem. Physics **7**, 1047 (1939); **9**, 76 (1941).
4. Cotton, F. A., and G. Wilkinson: Advanced inorganic chemistry. New York: Interscience Publishers 1966.
5. Crawford, Jr., B. L., and P. C. Cross: J. chem. Physics **6**, 595 (1938).
6. —, and W. Horowitz: J. chem. Physics **16**, 147 (1948).
7. Decius, J. C.: J. chem. Physics **17**, 1315 (1949).
8. Wadia, W., and L. S. Balloomal: Physic. Chem. of Glasses (forthcoming).
9. Biem, W.: Physic. Stat. Solidi **3**, 1927 (1963).
   Cochran, W., and G. S. Pawley: Proc. Roy. Soc. (London) A **280**, 1 (1964).
   Ludwig, W.: Recent developments in lattice theory. Tracts in Modern Physics **43**, p. 52. Berlin-Heidelberg-New York: Springer 1967.
10. Rosenthal, J. E.: Physic. Rev. **49**, 535 (1936).
    Dennison, D. M.: Rev. mod. Physics **12**, 175 (1940).

Dr. Wahby Wadia
Atomic Energy Establishment
Theoretical Physics Department
Cairo, Egypt, U.A.R.