

## POTENTIAL FIELD AND FORCE CONSTANTS OF CYANURIC FLUORIDE

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*(Received August 19, 1967; revised paper received August 29, 1968)*

The Wilson group theoretical method has been employed for the evaluation of potential energy constants for the planar and nonplanar vibrations of the cyanuric fluoride molecule possessing a planar cyclic structure with the symmetry point group  $D_{3h}$ . An orthonormalized set of symmetry coordinates satisfying the transformation properties has been constructed. A modified valence force field consisting of only eleven force constants has been applied and the force constants have been evaluated from the vibrational and structural data. The values of these force constants have been compared with those of the molecules having similar environments and chemical bonds with nearly identical internuclear distances. A brief discussion of the results has been given with special reference to the carbon-nitrogen and carbon-fluorine bonds.

*Introduction*

Cyanuric fluoride,  $C_3N_3F_3$ , a very reactive compound and a potentially useful starting material for a variety of chemical reactions has been subjected to very many spectral investigations. Grisley and his coworkers [1] studied the infrared absorption spectrum of this compound in liquid state and published their results without any comment. Steel and Ballreich [2] studied the infrared spectrum and assigned four of the strongest infrared bands. Later, the infrared spectrum of the basic structural unit, cyanogen fluoride, was studied and three fundamental frequencies were assigned by many investigators [3]. Through no physical evidence offers any specific conclusions on the structure, the chemical evidence [1], [6], of the possible models, favors a symmetric cyclic structure for the cyanuric fluoride molecule,  $C_3N_3F_3$ , with the symmetry point group  $D_{3h}$ . Recently, Griffiths and Irish [7] studied the Raman and infrared spectra with polarization measurements and assigned all of the active fundamental frequencies for cyanuric fluoride on the basis of a planar symmetric structure with the point group  $D_{3h}$ . It is aimed here on the basis of these recent Raman and infrared absorption spectra to evaluate the potential energy constants by the

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Wilson group theoretical method [8] employing a modified valence force field with only eleven valence force constants such that the results of the present investigation would be very useful for the evaluation of normal frequencies in other related molecules having similar chemical bonds.

### Symmetry coordinates

Since the chemical evidence [1], [6] favors a planar symmetric cyclic structure, the cyanuric fluoride molecule is characterized by three symmetry axes of which the  $z$  axis is perpendicular to the plane of the molecule, three vertical planes of symmetry ( $3\sigma_v$ ) each containing one carbon atom and one fluorine atom and a horizontal plane of symmetry ( $\sigma_h$ ) having all the atoms in its plane. The cyanuric fluoride molecule possessing a planar symmetric cyclic structure with the symmetry point group  $D_{3h}$  gives rise, according to the relevant symmetry considerations [9] to twenty one vibrational degrees of freedom constituting only fourteen fundamental frequencies. They are distributed under the various irreducible representations as follows:

$$3A'_1(R, p) + 2A'_2(\text{inactive}) + 5E'(R, p; I, ||) + 2A''_2(I, \perp) + 2E''(R, dp; I, \perp)$$

where  $R, I, p, dp, ||$  and  $\perp$  stand for Raman active, infrared active, polarized, depolarized, parallel vibration, and perpendicular vibration, respectively. The vibrations coming under the species  $E'$  and  $E''$  are the degenerate ones whereas those coming under the other species are the nondegenerate ones. The vibrational modes coming under the  $A''_2$  and  $E''$  species constitute the out-of-plane vibrations whereas those coming under the  $A'_1, A'_2,$  and  $E'$  species constitute the in-plane vibrations.

Eighteen internal coordinates have been selected here to describe the fifteen in-plane vibrational degrees of freedom and they are given as follows:  $\Delta r_1, \Delta r_2,$  and  $\Delta r_3$  are the carbon-fluorine stretching coordinates;  $\Delta d_1, \Delta d_2, \Delta d_3, \Delta d_4, \Delta d_5,$  and  $\Delta d_6$  are the carbon-

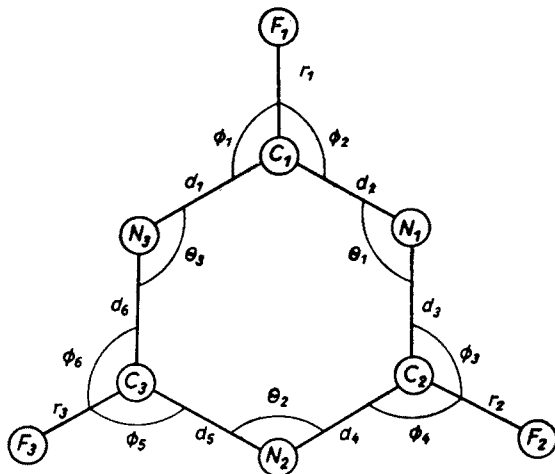


Fig. 1. Geometric illustration of the internal coordinates for the planar vibrations of cyanuric fluoride molecule. The symbols denote the values at the equilibrium configuration

nitrogen stretching coordinates;  $\Delta\theta_1$ ,  $\Delta\theta_2$ , and  $\Delta\theta_3$  are the carbon-nitrogen-carbon bending coordinates; and  $\Delta\Phi_1$ ,  $\Delta\Phi_2$ ,  $\Delta\Phi_3$ ,  $\Delta\Phi_4$ ,  $\Delta\Phi_5$  and  $\Delta\Phi_6$  are the nitrogen-carbon-fluorine bending coordinates (see Fig. 1). Hence, three redundancies are expected in constructing the symmetry coordinates from the internal coordinates describing the in-plane vibrations. Similarly, out-of-plane vibrations may also well be described. Nine internal coordinates (see Fig. 2) have been selected here to describe the six out-of-plane vibrational degrees of freedom and they are given as follows:  $\Delta\alpha_1$ ,  $\Delta\alpha_2$ ,  $\Delta\alpha_3$ ,  $\Delta\alpha_4$ ,  $\Delta\alpha_5$ ,  $\Delta\alpha_6$ ,  $\Delta\beta_1$ ,  $\Delta\beta_2$  and  $\Delta\beta_3$ . Hence, three redundancies are expected in constructing the symmetry coordinates from the

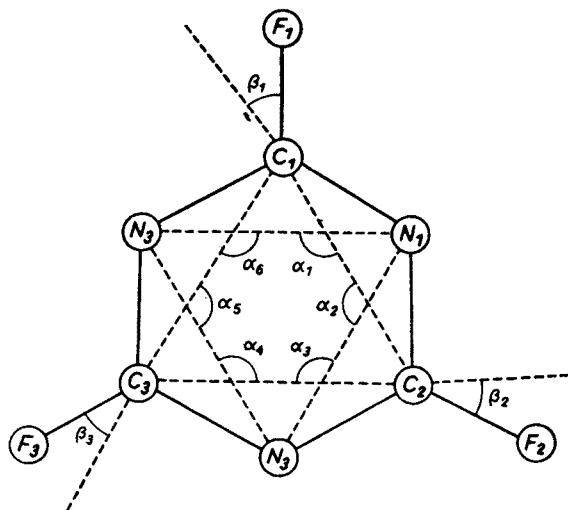


Fig. 2. Geometric illustration of the internal coordinates for the nonplanar vibrations of cyanuric fluoride molecule. The symbols denote the values at the equilibrium configuration

internal coordinates describing the out-of-plane vibrations. On the basis of the principle postulated by Wilson [8], a set of symmetry coordinates (linear combination of internal coordinates) satisfying the conditions of normalization, orthogonality, and transformations of the concerned vibration species has been constructed with help of the internal coordinates described above and they are given as follows:

For the  $A'_1$  type vibrations:

$$S_1 = (\Delta r_1 + \Delta r_2 + \Delta r_3) / \sqrt{3}$$

$$S_2 = (\Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4 + \Delta d_5 + \Delta d_6) / \sqrt{6}$$

$$S_3 = [ \sqrt{rd} (\Delta\Phi_1 + \Delta\Phi_2 + \Delta\Phi_3 + \Delta\Phi_4 + \Delta\Phi_5 + \Delta\Phi_6) + 2d (\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3) ] / \sqrt{18}$$

$$S_0 = [ (\Delta\Phi_1 + \Delta\Phi_2 + \Delta\Phi_3 + \Delta\Phi_4 + \Delta\Phi_5 + \Delta\Phi_6) - (\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3) ] / \sqrt{9} = 0 \text{ (redundant).}$$

For the  $A'_2$  type vibrations:

$$S_4 = (\Delta d_1 - \Delta d_2 + \Delta d_3 - \Delta d_4 + \Delta d_5 - \Delta d_6) / \sqrt{6}$$

$$S_5 = \sqrt{rd} (\Delta\Phi_1 - \Delta\Phi_2 + \Delta\Phi_3 - \Delta\Phi_4 + \Delta\Phi_5 - \Delta\Phi_6) / \sqrt{6}.$$

For the  $E'$  type vibrations:

$$S_{6a} = (2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6}$$

$$S_{6b} = (\Delta r_3 - \Delta r_2)/\sqrt{2}$$

$$S_{7a} = [2(\Delta d_1 + \Delta d_2) - (\Delta d_3 + \Delta d_4) - (\Delta d_5 + \Delta d_6)]/\sqrt{12}$$

$$S_{7b} = [(\Delta d_3 + \Delta d_4) - (\Delta d_5 + \Delta d_6)]/2$$

$$S_{8a} = [(\Delta d_3 - \Delta d_4) - (\Delta d_5 - \Delta d_6)]/2$$

$$S_{8b} = [2(\Delta d_1 - \Delta d_2) - (\Delta d_3 - \Delta d_4) - (\Delta d_5 - \Delta d_6)]/\sqrt{12}$$

$$S_{9a} = \sqrt{rd}[(\Delta\Phi_3 - \Delta\Phi_4) - (\Delta\Phi_5 - \Delta\Phi_6)]/2$$

$$S_{9b} = \sqrt{rd}[2(\Delta\Phi_1 - \Delta\Phi_2) - (\Delta\Phi_3 - \Delta\Phi_4) - (\Delta\Phi_5 - \Delta\Phi_6)]/\sqrt{12}$$

$$S_{10a} = [\sqrt{rd}\{2(\Delta\Phi_1 + \Delta\Phi_2) - (\Delta\Phi_3 + \Delta\Phi_4) - (\Delta\Phi_5 + \Delta\Phi_6)\} + 2d(\Delta\theta_1 + \Delta\theta_3 - 2\Delta\theta_2)]/6$$

$$S_{10b} = [2d(\Delta\theta_1 - \Delta\theta_3) - \sqrt{rd}(\Delta\Phi_3 + \Delta\Phi_4) + \sqrt{rd}(\Delta\Phi_5 + \Delta\Phi_6)]/\sqrt{12}$$

$$S_{0a} = [\sqrt{rd}\{2(\Delta\Phi_1 + \Delta\Phi_2) - (\Delta\Phi_3 + \Delta\Phi_4) - (\Delta\Phi_5 + \Delta\Phi_6)\} - d(\Delta\theta_1 + \Delta\theta_3 - 2\Delta\theta_2)]/\sqrt{18} = 0$$

(redundant)

$$S_{0b} = [-d\Delta\theta_1 + d\Delta\theta_3 - \sqrt{rd}(\Delta\Phi_3 + \Delta\Phi_4) + \sqrt{rd}(\Delta\Phi_5 + \Delta\Phi_6)]/\sqrt{6} = 0 \text{ (redundant).}$$

For the  $A_1''$  type vibration:

$$S_0 = d(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6)/\sqrt{6} = 0 \text{ (redundant).}$$

For the  $A_2''$  type vibrations:

$$S_{11} = d(\Delta\alpha_1 - \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4 + \Delta\alpha_5 - \Delta\alpha_6)/\sqrt{6}$$

$$S_{12} = \sqrt{rd}(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)/\sqrt{3}.$$

For the  $E''$  type vibrations:

$$S_{13a} = \sqrt{rd}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{6}$$

$$S_{13b} = \sqrt{rd}(\Delta\beta_2 - \Delta\beta_3)/\sqrt{2}$$

$$S_{14a} = d(\Delta\alpha_1 - \Delta\alpha_3 + \Delta\alpha_4 - \Delta\alpha_6)/2$$

$$S_{14b} = d(\Delta\alpha_1 - 2\Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 - 2\Delta\alpha_5 + \Delta\alpha_6)/\sqrt{12}$$

$$S_{0a} = d(\Delta\alpha_1 + 2\Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4 - 2\Delta\alpha_5 - \Delta\alpha_6)/\sqrt{12} = 0 \text{ (redundant)}$$

$$S_{0b} = d(\Delta\alpha_1 + \Delta\alpha_3 - \Delta\alpha_4 + \Delta\alpha_6)/2 = 0 \text{ (redundant).}$$

Here the angle displacements are multiplied by the equilibrium bond lengths  $r(\text{C}-\text{F})$  and  $d(\text{C}-\text{N})$  in order to keep the dimensions of the valence force constants referring to the angle bending the same as those of the force constants due to the bond stretching.

*Potential field and force constants*

In the most general harmonic potential energy expression for a molecule of the present study, the number of valence force constants is greater than the available number of fundamental frequencies. Even if the fundamental frequencies for the isotopic species are available, it is not possible to evaluate very uniquely all of the force constants. Hence, most of the interaction valence force constants of higher orders were neglected in this case by retaining only eleven valence force constants and the adopted modified valence force field for cyanuric fluoride is given as follows:

$$\begin{aligned}
 2V = & f_r[(\Delta r_1)^2 + (\Delta r_2)^2 + (\Delta r_3)^2] + \\
 & + f_d[(\Delta d_1)^2 + (\Delta d_2)^2 + (\Delta d_3)^2 + (\Delta d_4)^2 + (\Delta d_5)^2 + (\Delta d_6)^2] + \\
 & + 2f_{dd}[(\Delta d_1)(\Delta d_2) + (\Delta d_2)(\Delta d_3) + (\Delta d_3)(\Delta d_4) + (\Delta d_4)(\Delta d_5) + \\
 & \quad + (\Delta d_5)(\Delta d_6) + (\Delta d_6)(\Delta d_1)] + \\
 & + 2f_{rd}[(\Delta r_1)(\Delta d_1 + \Delta d_2) + (\Delta r_2)(\Delta d_3 + \Delta d_4) + (\Delta r_3)(\Delta d_5 + \Delta d_6)] + \\
 & + f_\phi d[(\Delta \Phi_1)^2 + (\Delta \Phi_2)^2 + (\Delta \Phi_3)^2 + (\Delta \Phi_4)^2 + (\Delta \Phi_5)^2 + (\Delta \Phi_6)^2] + \\
 & + 2f_{\phi\phi} d[(\Delta \Phi_1)(\Delta \Phi_2) + (\Delta \Phi_3)(\Delta \Phi_4) + (\Delta \Phi_5)(\Delta \Phi_6)] + \\
 & + f_\theta d^2[(\Delta \theta_1)^2 + (\Delta \theta_2)^2 + (\Delta \theta_3)^2] + \\
 & + 2f_{\theta\theta} d^2[(\Delta \theta_1)(\Delta \theta_2 + \Delta \theta_3) + (\Delta \theta_2)(\Delta \theta_3)] + \\
 & + f_\alpha d^2[(\Delta \alpha_1)^2 + (\Delta \alpha_2)^2 + (\Delta \alpha_3)^2 + (\Delta \alpha_4)^2 + (\Delta \alpha_5)^2 + (\Delta \alpha_6)^2] + \\
 & + 2f_{\alpha\alpha} d^2[(\Delta \alpha_1)(\Delta \alpha_3 + \Delta \alpha_5) + (\Delta \alpha_3)(\Delta \alpha_5) + (\Delta \alpha_2)(\Delta \alpha_4 + \Delta \alpha_6) + (\Delta \alpha_4)(\Delta \alpha_6)] + \\
 & + f_\beta r^2[(\Delta \beta_1)^2 + (\Delta \beta_2)^2 + (\Delta \beta_3)^2],
 \end{aligned}$$

where  $f_r$  is the valence force constant due to the C—F stretching;  $f_d$  is the force constant due to the C—N stretching;  $f_\phi$  is the force constant due to the N— $\hat{C}$ —F bending;  $f_\theta$  is the force constant due to the C— $\hat{N}$ —C bending;  $f_\alpha$  is the torsional force constant due to the interaction of the planes NCN and CNC along the C—N bonds;  $f_\beta$  is the out-of-plane bending force constant due to the perpendicular displacement of the fluorine atom out of the plane defined by the two adjacent C—N bonds; and all others are respective interaction force constants. In the above potential energy expression the angle displacements are being multiplied by the equilibrium interbond distances, namely,  $r$  and  $d$  in order to keep the dimensions of the valence force constants referring to the angle bending the same as those of the valence force constants due to the bond stretchings. By symmetry of the molecular system, the force constant due to the interaction of adjacent dihedral angles cannot be solved, the force constant due to the interaction of alternate dihedral angles inside the ring has been considered in the above potential energy expression.

The  $F$  matrix elements corresponding to potential energy matrices for the various irreducible representations were obtained by means of proper matrix multiplications according to the principles outlined by Wilson [8] and they are given as follows:  $F_{11} = f_r$ ,

$F_{22} = f_d + 2f_{dd}$ ,  $F_{12} = F_{21} = \sqrt{2}f_{rd}$ ,  $F_{33} = (1/3)(f_\phi + f_{\phi\phi}) + (2/3)(f_\theta + 2f_{\theta\theta})$ ,  $F_{66} = f_r$ ,  
 $F_{77} = (2f_d + f_{dd})/2$ ,  $F_{67} = F_{76} = -f_{rd}$ ,  $F_{88} = (2f_d - f_{dd})/2$ ,  $F_{99} = (f_\phi - f_{\phi\phi})$ ,  $F_{10\ 10}$   
 $= (1/3)(f_\phi + f_{\phi\phi}) + (2/3)(f_\theta - f_{\theta\theta})$ ,  $F_{11\ 11} = (f_\alpha + 2f_{\alpha\alpha})$ ,  $F_{12\ 12} = f_\beta$ ,  $F_{13\ 13} = f_\beta$ ,  $F_{14\ 14} = (f_\alpha - f_{\alpha\alpha})$ .  
 Since the vibrations corresponding to the frequencies  $\nu_4$  and  $\nu_5$  under the  $A'_2$  symmetry species are forbidden in both Raman and infrared spectra, the expressions for the symmetrized force constants  $F_{44}$ ,  $F_{55}$ , and  $F_{45}$  in terms of the valence force constants have not been given here, even though the symmetry coordinates under this  $A'_2$  species have been given above. All the other off-diagonal elements involving the interaction force constants have been, for the sake of convenience in solving the secular equations, neglected. The forces involved in the distortion of cyanuric fluoride are very similar to those of benzene ring. Thus,  $F_{11\ 11}$  and  $F_{11\ 12}$  of  $A'_2$  species are exactly similar to  $\beta$ , and  $-\eta$  in benzene as given by Miller and Crawford [10]. In a similar manner,  $F_{13\ 14}$  and  $F_{14\ 14}$  of  $E''$  species of cyanuric fluoride are equal to the  $\theta$  and  $\omega$  values as reported by Miller and Crawford [10]. This assumption was also made by Ferguson [11] in determining the force constants of 1,3,5-trifluorobenzene. The expressions for the off-diagonal elements of the symmetrized force constants have been, for the sake of comparison, given as  $F_{11\ 12} = \sqrt{2}(f_{\alpha\beta} - f'_{\alpha\beta} + f''_{\alpha\beta})$ ,  $F_{13\ 14} = (3/\sqrt{6})(f_{\alpha\beta} - f''_{\alpha\beta})$ . Thus, the force constants  $\beta$ ,  $\theta$ ,  $-\eta$ , and  $\omega$  from benzene are exactly carried over to the cyanuric fluoride molecule.

### Results

The observed fundamental frequencies in  $\text{cm}^{-1}$  for the cyanuric fluoride molecule reported by Griffiths and Irish [7] are given in Table I. Even though it has been clearly established [1], [6] that this molecule possesses a planar symmetrical structure with the symmetry point group  $D_{3h}$ , no structural data have either experimentally or theoretically been reported. However, it is quite reasonable to transfer such data to cyanuric fluoride from related heterocyclic compounds having similar chemical bonds. The values of inter-bond angles and carbon-nitrogen distance given by Lancaster and Stoicheff [12] for the s-triazine molecule have been transferred to cyanuric fluoride and their values are  $\theta = 113^\circ$ ,  $\phi = 116^\circ 30'$ , and  $d = 1.338 \text{ \AA}$ , respectively. A value  $1.34 \text{ \AA}$  has been considered for the C-F bond as it was used by Ferguson [11] for 1,3,5-trifluorobenzene. The fundamental equation  $|FG - E\lambda| = 0$  developed by Wilson [8] has been adopted here to construct the secular equations giving the normal frequencies in terms of the valence force constants where  $F$ ,  $G$ , and  $E$  represent the potential energy, kinetic energy, and unitary matrices and  $\lambda$  has been related to the normal frequency  $\nu$  in the form  $\lambda = 4\pi^2 c^2 \nu^2$ . Here  $c$  represents the velocity of light in vacuum. On the basis of the Wilson group theoretical method [8], the  $G$  matrix elements corresponding to the kinetic energy matrices were derived in accordance with the symmetry coordinates and molecular structural data given above. The secular equations giving the normal frequencies in terms of the valence force constants were constructed with help of the potential and kinetic energy matrices and the fundamental frequencies in  $\text{cm}^{-1}$  given in Table I. It is not possible to uniquely solve all the valence force constants and hence most of the interaction force constants of higher orders were neglected and the secular equations were solved. In solving the secular equations, the

values of force constants obtained from one species were transferred to another species in fixing the remaining force constants. The stretching force constants due to the C—N and C—F bonds are common in both the  $A'_1$  and  $E'$  species. Similarly the force constant  $f_\beta$  is common in both the  $A''_2$  and  $E''$  species. Such method of transferring force constants from one species to another in fixing the remaining force constants was adopted in easily solving the secular equations. The evaluated values of the valence force constants in  $10^5$  dynes/cm for the cyanuric fluoride molecule are given as follows:  $f_r = 6.125$ ,  $f_d = 6.708$ ,  $f_{dd} = 0.496$ ,  $f_{rd} = 0.443$ ,  $f_\theta = 0.484$ ,  $f_{\theta\theta} = 0.113$ ,  $f_\phi = 0.635$ ,  $f_{\phi\phi} = 0.187$ ,  $f_\alpha = 0.219$ ,  $f_{\alpha\alpha} = 0.026$ , and  $f_\beta = 0.226$ . The force constant due to the C—F stretching obtained here is not much deviated from the values for the same bond in other related molecules but there is a little change in the values of the force constant due to the C—N stretching. It is 6.708 in cyanuric fluoride whereas it is 6.7243 in *s*-triazine [13], and 6.8866 in pyrazine molecule [14]. All these values are more or less similar. The interaction force constant  $f_{dd}$  in cyanuric fluoride is 0.496 whereas it is 0.5134 in *s*-triazine [13] and 0.4698 in pyrazine [14]. The C— $\hat{N}$ —C bending force constant is 0.484 in cyanuric fluoride while it is 0.6524 in *s*-triazine [13] and 0.7421 in pyrazine [14]. This shows that there is a marked difference in the values of C— $\hat{N}$ —C bending force constant in all these heterocyclic compounds while there are similarities in the bond stretching and stretching interaction force constants. The out-of-plane bending force constant is 0.226 in cyanuric fluoride which is smaller than the values 0.2393 in *s*-triazine [13], 0.34 and 0.378 in benzene [15], [16], and 0.3946 in tropylium ion [17] but is greater than the value 0.1936 in pyrazine [18], thereby showing that the fluorine atom has greater freedom to move out of the plane in cyanuric fluoride than the hydrogen atom has in benzene and tropylium ion while the situation is reversed in the case of pyrazine. It is seen that the fluorine and hydrogen atoms move out of the plane formed by two nitrogen and one carbon atoms in cyanuric fluoride and *s*-triazine whereas the hydrogen atom moves from the plane formed by two carbon and one nitrogen atoms in pyrazine and the hydrogen atom moves from the plane formed by three carbon atoms in benzene and tropylium ion. In the case of nonplanar ring bendin deformation, it is seen that the force constant due to the torsion around the C—N bond in cyanuric fluoride is 0.219 while it is 0.2209 in *s*-triazine [13], and 0.2212 in pyrazine [18]. This shows that the torsion around the C—N bond is similar in all the heterocyclic compounds. The values of the force constants presented here for the cyanuric fluoride molecule would be very useful for the evaluation of normal frequencies in other related heterocyclic compounds as well highly complex molecules having similar chemical bonds.

This work was supported by a grant No DA-ARO-D-31-124-G864 from the U. S. Army Research Office — Durham and the authors are very much grateful to them for such financial support.

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