Vibrational Analysis of Polymeric Hydrogen Fluoride: Cyclic $(HF)_6$

S. J. Cyvin, V. Devarajan, J. Brunvoll, and Ø. Ra
Institute of Theoretical Chemistry, Technical University of Norway, Trondheim-NTH, Norway

(Z. Naturforsch. **28 a**, 1787—1793 [1973]; received 9 April 1973)

The molecular vibrations of cyclic $(HF)_6$ are studied. The consequences of complex characters for irreducible representations of the appropriate point group (C_{6h}) are elucidated. The secular equation of the vibrational problem is solved in terms of real coordinates. Those of the degenerate species were obtained by a transformation of the complex symmetry coordinates. The force constants were taken from solid HF data. Mean amplitudes of vibration were calculated and compared with electron diffraction results.

1. Introduction

The importance of hydrogen bonds in chemical and biological systems is well recognized, and this has stimulated the interest for the study of systems like polymeric HF. Special interest has been attached to the structural properties of HF polymers in the gas phase. The existence of $(HF)_n$ in vapours has been known since the work of Mallet[1]. The infrared spectrum of hydrogen fluoride polymers is reported probably for the first time by Imes[2], and the existence of $(HF)_6$ in the gas phase was suggested by Simons and Hildebrand[3]. The old structural studies have been reviewed very early[4,5]. In spite of this early evidence a long time has passed until the details of structural properties in $(HF)_n$ vapour became known with a degree of certainty, and several misleading conclusions have been drawn during this time.

The existence of different $(HF)_n$ species in vapour was demonstrated by a visual electron diffraction work[6]. However, the data were wrongly interpreted in favour of linear or nearly linear chains of different lengths, $(HF)_6$ being present as a predominant species. For this species in particular a hexagonal (cyclic) structure was discarded.

Many spectroscopic works on HF polymers have appeared. Several references[7–10] are found in the work of Smith[11], who has reported the temperature and pressure dependence of band absorbance in HF vapour systems[11,12]. Also some more recent works should be cited[13–15]. In one of these works[14] the data are interpreted in terms of a cyclic trimer structure in HF (g). This conclusion is disproved by Smith[15], who summarizes the situation in the following way: "With present experimental conditions, the apportioning of the absorption to particular polymers is difficult and uncertain"[15]. Consequently the above cited spectroscopic works have contributed little to precise assignments of vibrational frequencies to definite $(HF)_n$ species.

The most recently reported infrared work on gaseous $(HF)_n$, as far as we know, is furnished by Huong and Couzi[16]. These investigators have interpreted some spectral bands in terms of a cyclic hexamer and chain tetramer. They also claim evidence for the dimer almost without higher polymers under certain conditions. This work is a step towards a tentative assignment of frequencies to definite $(HF)_n$ species, but it is still far from a complete vibrational assignment. Besides the complications of unknown species in different proportions it should be pointed out that many frequencies are expected to be inactive in infrared. In the proposed planar cyclic $(HF)_6$ species, for instance, the selection rules prescribe only four frequencies out of twenty to be infrared-active.

Other modern investigations of HF polymers in the gaseous phase tend to conclude that the vapour at room temperature and below consists mainly of the monomer, dimer and hexamer[17,18]. A cyclic $(HF)_6$ molecule is believed to be the predominating polymeric species. The significant work of Janzen and Bartell[18] should be mentioned in particular. It is a modern sector gas electron diffraction work, in which precise interatomic distances for the cyclic $(HF)_6$ species are reported.

In the present work the molecular vibrations of a cyclic $(HF)_6$ model are treated theoretically for the first time. A normal coordinate analysis is performed using the force constants transferred from solid HF[19]. They reproduce quite well the solid infrared frequencies from Kittelberger and Hornig[20]. Calculated mean amplitudes of vibration[21] are re-

Reprint requests to Prof. Dr. S. J. Cyvin, Division of Physical Chemistry, University of Trondheim, *N-7034 Trondheim-NTH*, Norwegen.

ported in the present work. These quantities are believed to have some relevance to the electron diffraction measurements[18], in spite of the fact that the normal coordinate analysis is rather uncertain because of the lack of important spectroscopic data. On the other hand the present work may perhaps be helpful in future assignments of experimental vibrational frequencies.

2. Molecular Model

In their electron diffraction investigation Janzen and Bartell[18] conclude with a puckered rather than planar ring of the hexameric $(HF)_6$ structure in the *mean* distances it displays. They do not find sufficient information to distinguish boat from chair, or other, conformations. It is possible that a broad continuum of conformations is swept through as the exceedingly flexible ring vibrates. The mentioned investigators[18] also state that it is entirely possible, in view of the large vibrations involved, that the ring of fluorine atoms is planar in its *equilibrium* configuration. On the basis of this discussion it seems appropriate, at least as a starting point, to assume a planar $(HF)_6$ equilibrium structure in the vibrational analysis.

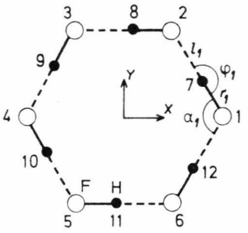

Fig. 1. The planar cyclic molecular model of $(HF)_6$; symmetry C_{6h}. One of each type of the in-plane valence coordinates is indicated.

The adopted molecular model is shown in Figure 1. It is a planar cyclic model of symmetry C_{6h}, and the F–H···F conformations are assumed to be linear. The structural parameters of $R(\text{F–H}) = 0.973$ Å and $D(\text{H}\cdots\text{F}) = (2.525 - 0.973)$ Å $= 1.552$ Å were taken from the data at $-19\,^{\circ}$C of the electron diffraction work[18].

The normal modes of vibration are distributed among the symmetry species of the C_{6h} group according to

$$\Gamma = 3\,A_g + 2\,B_g + E_{1g} + 4\,E_{2g} + A_u + 4\,B_u + 3\,E_{1u} + 2\,E_{2u}\,. \qquad (1)$$

These modes are separated into in-plane and out-of-plane vibrations according to:

$$\Gamma(\text{in-plane}) = 3\,A_g + 4\,E_{2g} + 4\,B_u + 3\,E_{1u}\,, \qquad (2)$$

$$\Gamma(\text{out-of-plane}) = 2\,B_g + E_{1g} + A_u + 2\,E_{2u}\,. \qquad (3)$$

3. Valence Coordinates

The vibrational analysis[22] is based on the following valence coordinates (see Fig. 1); $i = 1, 2, \ldots, 6$.

F–H stretchings, r_i, for atoms $i - (6+i)$.

H···F stretchings, l_i, involving H atoms number $6+i$.

HFH bendings, α_i, involving F atoms number i.

FHF in-plane linear bendings, φ_i, involving H atoms number $6+i$.

FHF out-of-plane linear bendings, γ_i, involving H atoms number $6+i$.

HFFH torsions, $\tau_1(12\text{–}1\text{–}2\text{–}8)$, $\tau_2(7\text{–}2\text{–}3\text{–}9)$, ..., $\tau_6(11\text{–}6\text{–}1\text{–}7)$.

The thirty-six valence coordinates specified above are not all independent; they contain six redundancies. When constructing the set of internal coordinates for the basis of the vibrational analysis (see below) the redundancies were removed simply by omitting certain combinations of valence coordinates under the appropriate species.

4. Non-Degenerate Symmetry Coordinates

Symmetry coordinates under the nondegenerate species are given in the following.

$$\begin{aligned} S_1(A_g) &= 6^{-1/2}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)\,, \\ S_2(A_g) &= 6^{-1/2}(l_1 + l_2 + l_3 + l_4 + l_5 + l_6)\,, \qquad (4) \\ S_3(A_g) &= (RD/6)^{1/2}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 + \varphi_6)\,; \end{aligned}$$

$$\begin{aligned} S_1(B_g) &= (RD/6)^{1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6), \\ S_2(B_g) &= (RD/6)^{1/2}(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4 + \gamma_5 - \gamma_6)\,; \end{aligned} \qquad (5)$$

$$S(A_u) = (RD/6)^{1/2}(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 + \gamma_5 + \gamma_6)\,; \qquad (6)$$

$$\begin{aligned} S_1(B_u) &= 6^{-1/2}(r_1 - r_2 + r_3 - r_4 + r_5 - r_6)\,, \\ S_2(B_u) &= 6^{-1/2}(l_1 - l_2 + l_3 - l_4 + l_5 - l_6), \qquad (7) \\ S_3(B_u) &= (RD/6)^{1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6), \\ S_4(B_u) &= (RD/6)^{1/2}(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4 + \varphi_5 - \varphi_6). \end{aligned}$$

5. Degenerate Real Internal Coordinates

A complete set of independent internal coordinates is produced by adding the following coordinates to those of Eqs. (4)—(7).

$$\mathfrak{S}_a(E_{1g}) = (RD/12)^{1/2}(\gamma_1 + 2\gamma_2 + \gamma_3 - \gamma_4 - 2\gamma_5 - \gamma_6); \tag{8}$$

$$\mathfrak{S}_b(E_{1g}) = \tfrac{1}{2}(RD)^{1/2}(\gamma_3 - \gamma_1 - \gamma_6 + \gamma_4); \tag{9}$$

$$\begin{aligned} \mathfrak{S}_{1a}(E_{2g}) &= 12^{-1/2}(r_1 - 2r_2 + r_3 + r_4 - 2r_5 + r_6), \\ \mathfrak{S}_{2a}(E_{2g}) &= 12^{-1/2}(l_1 - 2l_2 + l_3 + l_4 - 2l_5 + l_6), \\ \mathfrak{S}_{3a}(E_{2g}) &= (RD/12)^{1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6), \end{aligned} \tag{10}$$

$$\begin{aligned} \mathfrak{S}_{4a}(E_{2g}) &= (RD/12)^{1/2}(\varphi_1 - 2\varphi_2 + \varphi_3 + \varphi_4 - 2\varphi_5 + \varphi_6); \\ \mathfrak{S}_{1b}(E_{2g}) &= \tfrac{1}{2}(r_3 - r_1 + r_6 - r_4), \\ \mathfrak{S}_{2b}(E_{2g}) &= \tfrac{1}{2}(l_3 - l_1 + l_6 - l_4), \\ \mathfrak{S}_{3b}(E_{2g}) &= \tfrac{1}{2}(RD)^{1/2}(\alpha_3 - \alpha_2 + \alpha_6 - \alpha_5), \\ \mathfrak{S}_{4b}(E_{2g}) &= \tfrac{1}{2}(RD)^{1/2}(\varphi_3 - \varphi_1 + \varphi_6 - \varphi_4); \end{aligned} \tag{11}$$

$$\begin{aligned} \mathfrak{S}_{1a}(E_{1u}) &= \tfrac{1}{2}(r_1 - r_3 - r_4 + r_6), \\ \mathfrak{S}_{2a}(E_{1u}) &= \tfrac{1}{2}(l_1 - l_3 - l_4 + l_6), \\ \mathfrak{S}_{3a}(E_{1u}) &= \tfrac{1}{2}(RD)^{1/2}(\varphi_1 - \varphi_3 - \varphi_4 + \varphi_6); \end{aligned} \tag{12}$$

$$\begin{aligned} \mathfrak{S}_{1b}(E_{1u}) &= 12^{-1/2}(r_1 + 2r_2 + r_3 - r_4 - 2r_5 - r_6), \\ \mathfrak{S}_{2b}(E_{1u}) &= 12^{-1/2}(l_1 + 2l_2 + l_3 - l_4 - 2l_5 - l_6), \\ \mathfrak{S}_{3b}(E_{1u}) &= (RD/12)^{1/2}(\varphi_1 + 2\varphi_2 + \varphi_3 - \varphi_4 - 2\varphi_5 - \varphi_6); \end{aligned} \tag{13}$$

$$\begin{aligned} \mathfrak{S}_{1a}(E_{2u}) &= (RD/12)^{1/2}(\tau_1 - 2\tau_2 + \tau_3 + \tau_4 - 2\tau_5 + \tau_6), \\ \mathfrak{S}_{2a}(E_{2u}) &= (RD/12)^{1/2}(\gamma_1 - 2\gamma_2 + \gamma_3 + \gamma_4 - 2\gamma_5 + \gamma_6); \end{aligned} \tag{14}$$

$$\begin{aligned} \mathfrak{S}_{1b}(E_{2u}) &= \tfrac{1}{2}(RD)^{1/2}(\tau_3 - \tau_1 + \tau_6 - \tau_4), \\ \mathfrak{S}_{2b}(E_{2u}) &= \tfrac{1}{2}(RD)^{1/2}(\gamma_3 - \gamma_1 + \gamma_6 - \gamma_4). \end{aligned} \tag{15}$$

The real coordinates of Eqs. (8)—(15) are not true symmetry coordinates under the group C_{6h}. In the character table of this group there are complex numbers for the degenerate species[22]. Real and purely imaginary characters are obtained, however, by adding and subtracting the characters in the two rows pertaining to each of the degenerate species[22]. That is the clue to constructing a set of real internal coordinates in such cases. The above set (8)—(15) was constructed according to the pattern of symmetry coordinates under the D_{6h} group[21]. The fact that the real coordinates (8)—(15) are not true symmetry coordinates manifests itself by non-vanishing **G** matrix elements corresponding to *a* and *b* coordinates within the same species.

6. Group-Theoretical Background

Wigner's well known work on time-reversal symmetry and co-representations[23] furnishes a suitable theoretical setting for a treatment of complex symmetry coordinates and their recombination into real coordinates. (The term "time-reversal" actually relates to the time-dependent Schrödinger equation and is of no particular consequence in the present context.) With recourse to Wigner's analysis[23] we note that **GF** commutes with complex conjugation. The latter operation may conveniently be regarded as an anti-unitary operator, K_0, to be added to the set of point group operators. Hence the symmetry group $\mathscr{G}$ (in our case C_{6h}) may be extended to $\mathscr{G}' = \{\mathscr{G}, K_0\,\mathscr{G}\}$, where the original point group now plays the role of a subgroup of index 2. If an irreducible representation of $\mathscr{G}$ is non-equivalent to the corresponding complex conjugate representation (which obviously holds in our case), the attendant set of complex symmetry coordinates has to be extended by complex conjugation in order to provide an irreducible co-representation of the augmented group $\mathscr{G}'$. This way, an irreducible representation and its complex conjugate combine and become a degenerate species in terms of $\mathscr{G}'$. If the two ordinary representations are already degenerate (in terms of $\mathscr{G}$), then all frequency degeneracies are doubled. The enlarged set of symmetry coordinates (i.e. the original complex coordinates and their complex conjugates) relate to the vector space which carries the co-representation. In this space it is possible to choose a set of coordinate axes which yield real-valued coordinates. The point to note is that Wigner's theory guarantees that both constituents which are needed when constructing the co-representation are present in the usual decomposition into ordinary symmetry species. The above remarks also pertain to the case when an ordinary representation is equivalent to its complex conjugate (i.e. when they are related by a similarity transformation), but not equivalent to a real representation.

It seems worth mentioning that the combination of complex symmetry coordinates into real ones was employed long ago by Landau[24] in his investigation of second-order thermodynamic phase transitions. Landau refers to the combined species, i.e. the co-representation and its real coordinates, as a physically irreducible representation. Finally, the authors would be remiss not to mention that Lyubarskii[25] has described the combination of complex "cartesian" symmetry coordinates of molecules into real coordinates. However, that work has apparently passed largely unnoticed among molecular spectroscopists. Therefore we do not consider the present treatment in terms of valence coordinates to be superfluous.

7. Degenerate Symmetry Coordinates

In this section we are treating explicitly the complex symmetry coordinates which arise from the existence of complex characters for the C_{6h} group. They occur in the species E_{1g}, E_{2g}, E_{1u} and E_{2u}. The extension of Wilson's **GF** matrix method[22] to the general case of complex coordinates was formulated by Cyvin et al.[26] and applied to the C_{3h} model of boric acid[27,28]. Force constant analyses of the boric acid molecule[28,29] have been performed on the basis of this theory. In the present case of C_{6h} symmetry some of the essential features of the theory shall be illustrated by treating the E_{2u} species in some details.

True symmetry coordinates under the C_{6h} group are for example:

$$\begin{aligned} S_{1a}(E_{2u}) &= (RD/6)^{1/2}(-\tau_2+\varepsilon^*\tau_3+\varepsilon\tau_4-\tau_5 \\ &\qquad +\varepsilon^*\tau_6+\varepsilon\tau_1), \\ S_{2a}(E_{2u}) &= (RD/6)^{1/2}(-\gamma_2+\varepsilon^*\gamma_3+\varepsilon\gamma_4 \\ &\qquad -\gamma_5+\varepsilon^*\gamma_6+\varepsilon\gamma_1); \end{aligned} \tag{16}$$

$$\begin{aligned} S_{1b}(E_{2u}) &= (RD/6)^{1/2}(-\tau_2+\varepsilon\tau_3+\varepsilon^*\tau_4 \\ &\qquad -\tau_5+\varepsilon\tau_6+\varepsilon^*\tau_1), \\ S_{2b}(E_{2u}) &= (RD/6)^{1/2}(-\gamma_2+\varepsilon\gamma_3+\varepsilon^*\gamma_4 \\ &\qquad -\gamma_5+\varepsilon\gamma_6+\varepsilon^*\gamma_1). \end{aligned} \tag{17}$$

Here $\varepsilon = e^{i\pi/3}$, $\varepsilon^* = e^{-i\pi/3}$. The real coordinates of Eqs. (14) and (15) are connected with these symmetry coordinates through the unitary transformations

$$\begin{aligned} \mathfrak{S}_{na}(E_{2u}) &= 2^{-1/2}[S_{na}(E_{2u})+S_{nb}(E_{2u})], \\ \mathfrak{S}_{nb}(E_{2u}) &= 2^{-1/2}\,i[S_{na}(E_{2u})-S_{nb}(E_{2u})] \end{aligned} \tag{18}$$

for $n = 1, 2$.

Now we shall study the effect on the **G** and **F** matrices when the complex symmetry coordinates are transformed to the real set. Let this transformation be defined in matrix notation by

$$\mathfrak{S} = \mathbf{T}\,\mathbf{S}, \tag{19}$$

where $\mathfrak{S}$ and $\mathbf{S}$ represent the E_{2u} coordinates $\{\mathfrak{S}_{1a}, \mathfrak{S}_{2a}, \mathfrak{S}_{1b}, \mathfrak{S}_{2b}\}$ and $\{S_{1a}, S_{2a}, S_{1b}, S_{2b}\}$, respectively. Explicitly the transformation matrix of Eq. (19) reads

$$\mathbf{T} = 2^{-1/2}\begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ i & 0 & -i & 0 \\ 0 & i & 0 & -i \end{bmatrix} \tag{20}$$

or

$$\mathbf{T} = 2^{-1/2}\begin{bmatrix} \mathbf{E} & \mathbf{E} \\ \mathbf{i} & -\mathbf{i} \end{bmatrix}, \tag{21}$$

where

$$\mathbf{E} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \mathbf{i} = i\,\mathbf{E} = \begin{bmatrix} i & 0 \\ 0 & i \end{bmatrix}. \tag{22}$$

The above formulation is valid for the case of two degenerate pairs of coordinates in a given species. The theory is easily extended to any number, n, of degenerate pairs by assuming that the **E** and **i** submatrices of Eq. (21) are not restricted to being two-dimensional, but have the deimnsionality of n. The transformation (19) is unitary; hence

$$\mathbf{T}^{-1} = \mathbf{T}^{\dagger} = 2^{-1/2}\begin{bmatrix} \mathbf{E} & -\mathbf{i} \\ \mathbf{E} & \mathbf{i} \end{bmatrix}. \tag{23}$$

The complex **G** matrix in terms of the degenerate symmetry coordinates has the form

$$\mathbf{G} = \begin{bmatrix} \mathbf{H} & \mathbf{0} \\ \mathbf{0} & \mathbf{H}^* \end{bmatrix}. \tag{24}$$

Here the submatrix **H** (as well as the whole **G**) is Hermitian. The transformation according to Eq. (19) yields the corresponding real **G** matrix, $\mathfrak{G}$, which is based on the $\mathfrak{S}$ coordinates, by

$$\mathfrak{G} = \mathbf{T}\,\mathbf{G}\,\mathbf{T}^{\dagger}. \tag{25}$$

On inserting from Eqs. (21), (23) and (24) it is obtained

$$\begin{aligned} \mathfrak{G} &= \tfrac{1}{2}\begin{bmatrix} \mathbf{H}+\mathbf{H}^* & -i(\mathbf{H}-\mathbf{H}^*) \\ i(\mathbf{H}-\mathbf{H}^*) & \mathbf{H}+\mathbf{H}^* \end{bmatrix} \\ &= \begin{bmatrix} \mathrm{Re}(\mathbf{H}) & \mathrm{Im}(\mathbf{H}) \\ -\mathrm{Im}(\mathbf{H}) & \mathrm{Re}(\mathbf{H}) \end{bmatrix}. \end{aligned} \tag{26}$$

It is worth while looking at the form of the $\mathfrak{G}$ matrix in more details. In accord with Eq. (26) it may be written in general as

$$\mathfrak{G} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & \mathbf{A} \end{bmatrix}, \tag{27}$$

where $\mathbf{A}$ is symmetric, and $\mathbf{B}$ is skew-symmetric: $\mathbf{B}' = -\mathbf{B}$. The whole $\mathfrak{G}$ is of course symmetric. In the case of the E_{2u} species considered here the appropriate $\mathfrak{G}$ matrix block may be mapped in the following way.

$$\mathfrak{G} = \begin{bmatrix} A & B & 0 & C \\ B & A & -C & 0 \\ 0 & -C & A & B \\ C & 0 & B & A \end{bmatrix}. \tag{28}$$

In the same notation the complex $\mathbf{G}$ matrix, cf. Eq. (24), reads:

$$\mathbf{G} = \begin{bmatrix} A & B+iC & 0 & 0 \\ B-iC & A & 0 & 0 \\ 0 & 0 & A & B-iC \\ 0 & 0 & B+iC & A \end{bmatrix}. \tag{29}$$

The actual numerical values of A, B and C are found in Table 1. The table shows numerically all the $\mathbf{G}$ matrix elements of the present analysis.

The transformation of the force-constant matrix from the complex $\mathbf{F}$ into the real $\mathfrak{F}$ follows exactly the same pattern as that of the $\mathbf{G}$ matrix. Hence the real $\mathfrak{F}$ matrix possesses the same form as indicated by Eqs. (26) and (27).

In conclusion of this discussion it should be clear that the solution of the secular equation of molecular vibrations[22] in terms of the real matrices is equivalent to a well-known method of treating complex matrices. In this treatment a complex $n \times n$ matrix is represented by a real $2n \times 2n$ matrix[19, 30, 31].

8. Harmonic Force Field

Following Tubino and Zerbi[19] we have constructed a seven-parameter harmonic potential functio viz.

$$2\,V = \sum_{i=1}^{6} K_r r_i^2 + 2\,F\,r_i r_{i+1} + K_l l_i^2 + H_\alpha \alpha_i^2 + H_\varphi \varphi_i^2 + H_\gamma \gamma_i^2 + H_\tau \tau_i^2 . \tag{30}$$

Here the term with F pertains to next-neighbour (F–H, F–H) interaction; hence $r_7 \equiv r_1$. Because of the lack of an experimental assignment of $(HF)_6(g)$ frequencies we have transferred the valence force constants from solid HF, as developed by Tubino and Zerbi[19].

Table 1. $\mathbf{G}$ (or $\mathfrak{G}$) matrix elements (Amu^{-1}) in terms of the real $\mathbf{S}$ (or $\mathfrak{S}$) coordinates.

Species A_g

1	1.045		
2	− 1.018	1.045	
3	− 0.036	− 0.058	4.358

Species B_g

1	0.937	
2	1.196	4.200

Species E_{1g}

a	4.358	
b	0.000	4.358

Species E_{2g}

1 *a*	1.045							
2 *a*	− 0.979	1.045						
3 *a*	− 0.018	− 0.029	1.382					
4 *a*	0.018	0.029	2.179	4.279				
1 *b*	0.000	0.023	0.031	0.031	1.045			
2 *b*	− 0.023	0.000	− 0.050	− 0.050	− 0.979	1.045		
3 *b*	− 0.031	0.050	0.000	0.876	− 0.018	− 0.029	1.382	
4 *b*	− 0.031	0.050	− 0.876	0.000	0.018	0.029	2.179	4.279

Species A_u

4.410

Species B_u

1	1.045			
2	− 0.966	1.045		
3	− 0.036	0.058	0.390	
4	0.036	0.058	1.011	4.252

Species E_{1u}

1 *a*	1.045					
2 *a*	− 1.005	1.045				
3 *a*	− 0.018	− 0.029	4.331			
1 *b*	0.000	− 0.023	− 0.031	1.045		
2 *b*	0.023	0.000	0.050	− 1.005	1.045	
3 *b*	0.031	− 0.050	0.000	− 0.018	− 0.029	4.331

Species E_{2u}

1 *a*	4.748			
2 *a*	0.605	4.252		
1 *b*	0.000	− 4.358	4.748	
2 *b*	4.358	0.000	0.605	4.252

They are: $K_r = 5.424$ mdyne Å^{-1}, $F = -0.321$ mdyne Å^{-1}, $K_l = 0.537$ mdyne Å^{-1}, $H_\varphi = 0.199$ mdyne Å, $H_\gamma = 0.061$ mdyne Å, and $H_\tau = 0.001$ mdyne Å. Let this potential function be given in matrix notation by

$$2\,V = \mathbf{R}'\,\mathbf{f}\,\mathbf{R}\,. \tag{31}$$

The thirty-six valence coordinates are not independent: they contain six redundancies. But all these coordinates may be expressed in a unique way in terms of a set of thirty independent internal coordinates:

$$\mathbf{R} = \mathbf{W}\,\mathbf{S}\,. \tag{32}$$

Here $\mathbf{S}$ is supposed to represent the set of internal coordinates given by Eqs. (4)—(15). Then the force-constant matrix in terms of the $\mathbf{S}$ coordinates may be found according to the transformation

$$\mathbf{F} = \mathbf{W}'\,\mathbf{f}\,\mathbf{W}\,. \tag{33}$$

It is emphasized that the relation (33) does not imply any inversion of $\mathbf{W}$, only a transpose of this matrix. Since $\mathbf{W}$ is a rectangular (36×30) matrix it cannot be inverted. The transformation matrix $\mathbf{W}$ is conveniently computed by means of Wilson's $\mathbf{S}$ vectors[22], which are contained in the transformation matrices of[21, 22]

$$\mathbf{R} = \mathbf{b}\,\mathbf{x} \tag{34}$$

and

$$\mathbf{S} = \mathbf{B}\,\mathbf{x}\,. \tag{35}$$

The transformation matrix of Eqs. (32) and (33) is given by

$$\mathbf{W} = \mathbf{b}\,\mathbf{m}^{-1}\,\mathbf{B}'\,\mathbf{G}^{-1}\,, \tag{36}$$

where $\mathbf{m}$ is the $(3N \times 3N)$ diagonal matrix of atomic masses.

The procedure outlined above was used to express the potential energy in terms of the $\mathbf{F}$ matrix. The numerical result is reported in Table 2.

9. Normal Coordinate Analysis

The secular equation[22] was solved in terms of the $\mathbf{S}$ coordinates using the (real) $\mathbf{G}$ and $\mathbf{F}$ matrices of Tables 1 and 2, respectively. In the degenerate species each frequency value came out twice, as it should be according to the theory. The calculated frequencies are shown in Table 3.

10. Mean Amplitudes of Vibration

The force field was used to calculate the mean amplitudes of vibration according to well-established methods[21]. Table 4 shows the results at the temper-

Table 2. $\mathbf{F}$ (or $\mathfrak{F}$) matrix elements (mdyne Å^{-1}) in terms of the real $\mathbf{S}$ (or $\mathfrak{S}$) coordinates.

Species A_g			
1	4.782		
2	0.000	0.537	
3	0.000	0.000	0.143

Species B_g		
1	0.000662	
2	0.000	0.0404

Species E_{1g}		
a	0.0411	
b	0.000	0.0411

Species E_{2g}								
1 a	5.745							
2 a	0.000	0.537						
3 a	0.000	0.000	0.0113					
4 a	0.000	0.000	0.000	0.132				
1 b	0.000	0.000	0.000	0.000	5.745			
2 b	0.000	0.000	0.000	0.000	0.000	0.537		
3 b	0.000	0.000	0.000	0.000	0.000	0.000	0.0113	
4 b	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.132

Species A_u	
	0.0404

Species B_u				
1	6.066			
2	0.000	0.537		
3	0.000	0.000	0.0113	
4	0.000	0.000	0.000	0.132

Species E_{1u}						
1 a	5.106					
2 a	0.0027	0.540				
3 a	−0.0047	−0.0047	0.140			
1 b	0.000	0.000	0.0006	5.106		
2 b	0.000	0.000	0.0006	0.0027	0.540	
3 b	−0.0006	−0.0006	0.000	−0.0047	−0.0047	0.140

Species E_{2u}				
1 a	0.000662			
2 a	0.000	0.0404		
1 b	0.000	0.000	0.000662	
2 b	0.000	0.000	0.000	0.0404

Table 3. Calculated frequencies (cm^{-1}) for cyclic $(HF)_6$ (g).

Species	Wave number	Activity *
A_g	3065	Ra
	1029	Ra
	203	Ra
B_g	537	ia
	26	ia
E_{1g}	551	Ra
E_{2g}	3322	Ra
	991	Ra
	327	Ra
	33	Ra
A_u	550	IR
B_u	3403	ia
	979	ia
	356	ia
	53	ia
E_{1u}	3153	IR
	1017	IR
	252	IR
E_{2u}	545	ia
	15	ia

* Ra = Raman active, IR = infrared active, ia = inactive.

atures of absolute zero, −19 °C and +25 °C. The interatomic distance separations (in Å) as calculated from the adopted structural parameters are included in the table in order to facilitate the identification of the various types of distances.

The electron diffraction work[18] already furnishes some experimental mean amplitudes, which may be compared with the present calculations. For the FF distances at −19 °C the observed values are $(F_1 \cdots F_2)$ 0.089 ± 0.003 Å, $(F_1 \cdots F_3)$ 0.39 ± 0.06 Å and $(F_1 \cdots F_4)$ 0.33 ± 0.08 Å. The two first values are compatible with the present calculations, which give (see also Table 4) 0.093 and 0.421 Å for $F_1 \cdots F_2$ and $F_1 \cdots F_3$, respectively. For $F_1 \cdots F_4$ the calculated value is 0.587 Å, which is significantly larger than the observed value. We have no good explanation for this discrepancy. For the FH bond distance the mean amplitude from electron diffraction is reported to be[18] 0.066 Å (as in the monomer), which is somewhat smaller than the calculated value of 0.074 Å (see Table 4).

Table 4. Calculated mean amplitudes of vibration (Å) for cyclic $(HF)_6$.

Distance	0 °K	−19 °C	25 °C
$F_1 \ldots H_7$ (0.973)	0.074	0.074	0.074
$H_7 \ldots F_2$ (1.552)	0.099	0.111	0.115
$F_1 \ldots F_2$ (2.525)	0.076	0.093	0.099
$F_1 \ldots F_3$ (4.373)	0.151	0.421	0.455
$F_1 \ldots F_4$ (5.050)	0.186	0.587	0.635
$F_1 \ldots H_8$ (3.127)	0.142	0.254	0.271
$H_7 \ldots F_3$ (3.564)	0.156	0.337	0.363
$F_1 \ldots H_9$ (4.480)	0.191	0.449	0.484
$H_7 \ldots F_4$ (4.641)	0.198	0.498	0.536
$H_7 \ldots H_8$ (2.206)	0.152	0.239	0.253
$H_7 \ldots H_9$ (3.821)	0.197	0.357	0.381
$H_7 \ldots H_{10}$ (4.412)	0.218	0.421	0.450

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