

## Force field study of chloryl fluoride ( $\text{ClO}_2\text{F}$ ) using Green's function procedure

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**Abstract.** An attempt has been made to apply Green's function and partitioning technique to the case of  $\text{XY}_2\text{Z}$  ( $\text{ClO}_2\text{F}$ ) pyramidal type molecule belonging to  $C_s$  point group. The isotopic rules have been formulated. The force constants, rotation distortion constants and mean amplitude of vibration have been computed and compared with other observed and calculated values whichever is available.

**Keywords.** Green's function procedure; mixing parameter; isotopic rules; force constants; chloryl fluoride  $\text{ClO}_2\text{F}$ .

### 1. Introduction

The use of Green's function for the vibrational analysis of substituted and perturbed molecules was developed by DeWames and Wolfram (1964a, b; 1966a, b). The solution of the isotopic Green's function equation can become a sizeable task for more complicated cases of an unsymmetrical molecule. Also difficulties arise when solving higher order secular determinants. In the case of species containing four vibrational modes ambiguities arise in generating the mixing parameter matrix ( $A$ ) and further complications arise in solving them. For  $\text{XYZ}$  bent type molecules, belonging to  $C_s$  point group this procedure was successfully applied by Ramaswamy and Namasivayam (1970). In the present study the isotopic rules of the unsymmetrical pyramidal chloryl fluoride molecule belonging to  $C_s$  point group were derived along with other molecular constants using Green's function procedure. The isotopic product rules were verified.

### 2. Isotopic rules for $\text{XY}_2\text{Z} \rightarrow \text{X}'\text{Y}_2\text{Z}$ molecule

Unsymmetrical  $\text{XY}_2\text{Z}$  type molecule is having six distinct vibrational modes. They fall into the irreducible representation  $4A' + 2A''$ . The isotopic rules for the two vibrational species were derived by solving the secular determinant (DeWames and Wolfram 1964b)

$$|\epsilon \omega^2 G(\omega)^2 + I| = 0 \quad (1)$$

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where  $G(\omega)^2$  is the Green's function of the unperturbed molecule,  $\omega$  is the frequency of vibration and  $I$  — the identity matrix and  $\epsilon = (m_a^i - m_a)/m_a$ . Here  $m_a^i$  is the mass of the substituted atom and  $m_a$  is the mass of original atom. The determinant equation is automatically separated out according to the irreducible representation of the molecule. The Green's function is related to the matrix of transformation  $l$  between the normal and mass weighted Cartesian coordinates. To obtain  $l$  a set of orthogonalized Cartesian symmetry coordinates  $S$  which include rotations and translations were constructed. A linear combination of these symmetry coordinates with 'proper mixing parameter' will yield a set of normal coordinates

The main difficulty lies in the determination of the proper combination of symmetry coordinates with suitable mixing parameters to represent actual normal modes of vibration in a single species. In  $A'$  species there are four symmetry coordinates and by using them we can write number of sets of normal coordinates. But only one of them will be proper and true set and will give the real solution of this species. The following set is chosen:

$$\begin{aligned} Q_1 &= (S_1 + pS_3)/\sqrt{1 + p^2} \\ Q_2 &= (S_2 + qS_4)/\sqrt{1 + q^2} \\ Q_3 &= (S_3 - pS_1)/\sqrt{1 + p^2} \\ Q_4 &= (S_4 - qS_2)/\sqrt{1 + q^2} \end{aligned} \quad (2)$$

Here  $p$  and  $q$  are mixing parameters and they cannot be determined independently. Hence one of the values,  $p$  is taken as unity as a first approximation (Ramaswamy and Shanmugam 1973). This set (eq. 2) gave consistent values for the mixing parameters and gave a very good fit for the various equations involving the isotopic sum rule and product rules.

The normal coordinates for  $A''$  species are as follows :

$$Q_5 = (S_5 + t S_6)/\sqrt{1 + t^2} \quad (3)$$

$$Q_6 = (S_6 - t S_5)/\sqrt{1 + t^2} \quad (4)$$

where  $t$  is the mixing parameter. In eqs (2), (3) and (4)  $Q$  and  $S$  represent the normal coordinates and Cartesian symmetry coordinates respectively. The six translational and rotational coordinates are themselves normal coordinates.

The frequencies of the isotopically substituted  $X^i Y_2 Z$  molecule can be obtained from eq. (1) and the perturbation associated with three rows of the  $l$  matrix representing  $X$  atom. The resulting determinant in the present case reduces to

$$\begin{aligned} & \{ [\epsilon\omega^2 G_{11}(\omega^2) + 1] \{ [\epsilon\omega^2 G_{33}(\omega^2) + 1] - \{\epsilon\omega^2 G_{13}(\omega^2)\}^2 \} \\ & \times [\epsilon\omega^2 G_{22}(\omega^2) + 1] \} = 0. \end{aligned} \quad (5)$$

Considering the fact that  $G_{13}(\omega^2) = G_{31}(\omega^2)$  and all other  $G_{ij}$ s zero. From eq. (5) we get two equations which are independently equal to zero. The solution of these equations give the frequencies corresponding to the species of isotopically substituted molecule. As the isotopic rule obtained here is complicated because of the poor symmetry of the molecule, they are given in appendix\* in an abbreviated or with suitable contractions. The product rules are verified in all cases.

\* This can be had from the authors on request.

### 3. Spectral data and structural parameters

The infrared spectrum of chloryl fluoride with assignments of the fundamental frequencies on the basis of pyramidal model has been reported by Arvia and Aymonino (1963). Raman spectrum was recorded and line polarization was established by Smith *et al* (1964). The symmetry coordinates and assignments used here are identical with Smith *et al* (1964). The structural parameters are from Charles and Gerry (1974). The inverse kinetic energy matrix is constructed using Wilson's  $S_{kt}$  vectors (1955) and it is essentially the same as that obtained by Cotton and Horrocks (1960). The frequency and the structural parameters are given in table 1.

### 4. Molecular constants

#### 4.1. The potential energy constants

The potential energy constants  $F$  can be obtained from the matrix relation given by DeWames and Wolfram (1966b).

$$F = \tilde{B}^{-1} A \Lambda \tilde{A} B^{-1} \quad (6)$$

where  $\Lambda = 4\pi^2 c^2 \omega^2$  and  $A$  is the mixing parameter matrix,  $c$ —the velocity of light. The  $B$  matrix can be computed from the relation

$$B = (UDS)_{\text{truncated}} \quad (7)$$

where  $U$  is the matrix of transformation between internal symmetry and internal coordinates.  $D$  is the matrix of transformation between internal and Cartesian coordinates. The potential energy constants are computed from relation (6) and the valence force constants deduced from them are presented in table 2.

Table 1. Vibration frequencies and structural parameters.

		Vibration frequencies in $\text{cm}^{-1}$ by Smith <i>et al</i> (1964)		Structural parameters Charles and Gerry (1974)
		$^{35}\text{ClO}_2\text{F}$	$^{37}\text{ClO}_2\text{F}$	
$A'$	1	1105.8	1098.4	$r(\text{Cl-O}) = 1.418 \text{ \AA}$
	2	630.2	621.6	$R(\text{Cl-F}) = 1.697 \text{ \AA}$
	3	546.5	543.0	$\alpha(\text{O-Cl-F}) = 101^\circ 72'$
	4	402.6	400.2	$\beta(\text{O-Cl-O}) = 115^\circ 14'$
$A''$	5	1271.0	1258.6	
	6	367.0	365.8	

Table 2. Valence force constants (mdynes/Å).

	Present work	Smith <i>et al</i> (1964)	Robinson <i>et al</i> (1969)
$f_r$	8.9971*	9.07	10.08
$f_R$	3.3616	2.53	3.34
$f_a$	0.5896	0.59	0.62
$f_\beta$	0.9590	1.06	1.09
$f_{Rr}$	0.2177	0	0.62
$f_{rr}$	0.0706	-0.12	-0.43
$f_{r\beta}$	0.1407	0.38	0.84
$f_{ra}$	0.0407	-0.10	0.89
$f_{ra'}$	0.0986	0.10	-0.50
$f_{R\beta}$	-0.1316	0	-0.13
$f_{Ra}$	0.2319	0	0.37
$f_{aa}$	0.0994	0.13	0.04
$f_{a\beta}$	0.0318	0.14	0.12

\* This number of significant figures in the present work is retained to secure internal consistency in the calculations.

#### 4.2. Rotation distortion constant

The rotation distortion parameters  $\tau_{\alpha\beta\gamma\delta}$  can be obtained from the theoretical formulation for vibration-rotation interaction by Kivelson and Wilson (1952). The parameters are defined as

$$\hbar^4 \tau_{\alpha\beta\gamma\delta} = - \frac{K}{I_{\alpha\alpha}^0 I_{\beta\beta}^0 I_{\gamma\gamma}^0 I_{\delta\delta}^0} \sum \frac{a_i^{\alpha\beta} a_i^{\gamma\delta}}{\omega_i^2} \quad (8)$$

where  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are in turn  $x$ ,  $y$  or  $z$ . If these parameters are expressed in MHz the constant  $K$  has the value  $5.7498 \times 10^9$  and the vibrational frequencies are in  $\text{cm}^{-1}$ . The principal components of moment of inertia tensor  $I_{\alpha\alpha}^0$  are evaluated for the ground state and in the centre of mass of the molecule and the coefficients  $a_i^{\alpha\beta}$  are related to  $l$  matrix (Oka and Morino 1961; Alti *et al* 1965) and they are evaluated by the procedure given by Savariraj and Jayapandian (1971). Then the rotation distortion constants  $D_J$ ,  $D_K$ ,  $D_{JK}$ , and  $\delta_J$  are evaluated and given in table 3.

#### 4.3. Mean amplitude of vibration

The mean square amplitude matrix ( $\Sigma$ ) were obtained using Cyvin's (1958) relation. The mean square amplitudes for non-bonded atom pairs were calculated by the method of Ramaswamy *et al* (1962). The mean amplitude quantities computed from  $\Sigma$  elements are given in table 4.

### 5. Results and discussion

The isotopic rules obtained here using Green's function approach are similar to that of Teller-Redlich product rule (Redlich 1935; Herzberg 1945) and are derived without assuming force field model.

Table 3. Rotation distortion constants (MHz).

	Present work	Observed values Charles and Gerry (1974)
$D_J$	$1.0297 \times 10^{-2}$ *	$0.90 \pm 0.18 \times 10^{-2}$
$D_K$	$-4.3901 \times 10^{-3}$	$-3.10 \pm 0.15 \times 10^{-3}$
$D_{JK}$	$-5.6495 \times 10^{-3}$	$-4.5 \pm 0.06 \times 10^{-3}$
$\delta_J$	$1.1016 \times 10^{-3}$	$1.06 \pm 0.004 \times 10^{-3}$

\* This number of significant figures in the present work is retained to secure internal consistency in calculations.

Table 4.  $\Sigma$  matrix elements ( $\text{\AA}$ )<sup>2</sup> and mean amplitude of vibration ( $\text{\AA}$ ) at 298.16° K.

$\Sigma$	Present work ( $\text{\AA}$ ) <sup>2</sup> $\times 10^{-8}$		Mean amplitude of vibration ( $\text{\AA}$ )	
			Present work for $\text{ClO}_2\text{F}$	Muller <i>et al</i> (1968) for $\text{ClO}_2\text{F}$
$\Sigma_{11}$	1.2204	$\sigma_r$	0.0362	0.0356
$\Sigma_{22}$	2.5714	$\sigma_R$	0.0507	0.0446
$\Sigma_{33}$	3.2242	$\sigma_a$	0.0425	
$\Sigma_{44}$	4.1994	$\sigma_\beta$	0.0400	
$\Sigma_{12}$	0.1242	$\sigma_{O \cdots O}$	0.0553	0.056
$\Sigma_{13}$	-0.2971	$\sigma_{O \cdots F}$	0.0694	0.065
$\Sigma_{14}$	-0.0479			
$\Sigma_{23}$	0.3769			
$\Sigma_{24}$	-1.4429			
$\Sigma_{34}$	0.3425			
$\Sigma_{55}$	1.3942			
$\Sigma_{66}$	4.4736			
$\Sigma_{56}$	-0.1267			

\* This number of significant figures in the present work is retained for internal consistency in calculations.

The Cl-O stretching force constant ( $f_r$ ) 8.9971 mdyn/ $\text{\AA}$  compares well with the value of 9.07 mdyn/ $\text{\AA}$  of Smith *et al* (1964). This value is also due to  $p - d\pi$  bonding as suggested by So and Chau (1973a, b). According to Smith *et al* (1964) there is a mixing between the Cl-F stretching and O-Cl-F bending modes. Using this mixing, the Green's function technique leads to the Cl-F stretching force constant value ( $f_R$ ) 3.3616 mdyn/ $\text{\AA}$ . This agrees with the value of 3.34 mdyn/ $\text{\AA}$  of Robinson *et al* (1969). The present value of  $f_R$  is in agreement with

the value of the molecules having similar bond (Muller *et al* 1968; Ramaswamy and Muthusubramanian 1971a, b). According to Robinson *et al* (1969) the present value represents group vibration. However the present value is higher than the value of Smith *et al* (1964). O-Cl-F bending force constant ( $f_a$ ) 0.5896 mdyn/Å and O-Cl-O bending force constant ( $f_b$ ) 0.9590 mdyn/Å agree well with the reported values as seen from table 2. Regarding the interaction-force constants the agreement is generally good. However, there is a slight difference between the values of the present work and the earlier reported ones. In the previous methods some constraints were used for frequency fit. Green's function procedure is independent of any force field model and no constraint is involved here. This may be the reason for the slight differences particularly in interaction force constants.

The rotation distortion constants are generally in good agreement with the experimental values reported by Charles and Gerry (1974) and they are presented in table 3. Experimental data were not available for direct comparison of mean amplitude of vibration. Therefore it is compared with the molecule perchloryl fluoride (ClO<sub>3</sub>F) having a similar bond. The values are reported in table 4.

Hence it may be concluded that the method of Green's function procedure can be applied to determine a reasonable set of molecular constants for molecules of higher order with lower symmetry like chloryl-fluoride.

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