

Electron diffraction data as a constraint in the determination of force field of thallos halide dimers

D K SHARMA, U P VERMA, A N PANDEY and V KUMAR*

Molecular Spectroscopy Research Laboratory, Department of Physics, Meerut College, Meerut 250001

*M.M. College, Modinagar 201204

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Abstract. Electron diffraction data have been used as a constraint in the determination of force field for Tl_2F_2 having planar rhombic structure. The L-F approximation method, recently given by us, has also been applied to evaluate force constants for thallos halide dimers, e.g. Tl_2F_2 and Tl_2Cl_2 . The results have been compared with the available experimental data in order to check the validity of the present work. It is concluded that non-bond experimental mean amplitude $U_{T_1 \dots T_1}$ for Tl_2F_2 is capable of fixing the force field and L-F approximation gives reasonably good force fields for the two thallos halide dimers now under study.

Keywords. Force constants of Tl_2F_2 , Tl_2Cl_2 ; Force fields for Tl_2X_2 ($X = F, Cl$); thallos halide.

1. Introduction

Recently, Lesiecki and Nibler (1975) have studied infrared and Raman spectra for monomeric and dimeric thallos halide species isolated in argon matrices and concluded that both Tl_2F_2 and Tl_2Cl_2 molecules have planar rhombic structures rather than linear configurations as proposed on the basis of mass spectroscopy, infrared, and photoelectron studies. Since the electron diffraction results for Tl_2F_2 are also available in literature (Solomonik *et al* 1974), it was considered worthwhile to use this data as a constraint in the study of force field for Tl_2F_2 . Recently Pandey *et al* (1976) have given L-F approximation method to solve 2×2 secular determinant occurring in molecular dynamics. In the present work evaluation of the force constants for Tl_2F_2 and Tl_2Cl_2 by L-F approximation method is attempted and these results are compared with the data obtained by using electron-diffraction.

2. Theoretical considerations

Planar rhombic X_2Y_2 type molecule belongs to D_{2h} point group and fundamental frequencies are distributed among different species as:

$$\Gamma = 2A_g + B_{1g} + B_{1u} + B_{2u} + B_{3u}.$$

By making use of appropriate symmetry coordinates (Lesiecki and Nibler 1975

and taking into account the central forces, the following relationship has been derived for the non bond mean-square amplitude:

$$U^2_{\gamma \dots \gamma} = \langle S_{22}^2 \rangle = \langle \Delta R^2 \rangle = \Sigma_{22}(A_\rho),$$

where ΔR stands for changes in equilibrium non-bond distance. The remaining symmetrized mean-square amplitude elements, e.g., $\Sigma_{11}(A_\rho)$ and $\Sigma_{12}(A_\rho)$ have been obtained by inserting the experimental value of $\Sigma_{22}(A_\rho)$ in the Cyvin's secular equation (Cyvin 1959)

$$|\Sigma G^{-1} - \Delta E| = 0.$$

where G^{-1} is the inverse kinetic energy matrix. In this way we get all the Σ elements of A_ρ species. The three symmetrized F -elements have been evaluated with the help of the following equations:

$$\det |GF - \lambda E| = 0$$

and

$$\det |\Sigma F - \lambda \Delta E| = 0$$

where the symbols have their usual meanings (Cyvin 1968).

In order to compute the three symmetrized force constants under A_ρ species the L-F approximation method (Pandey *et al* 1976, Sharma *et al* 1976) has been used. The method has been formulated on the ground that the magnitude of the square of the non-diagonal elements L_{ij} and F_{ij} of the L and F matrices are very small compared to L_{ii} and F_{ii} . The method is given below:

The most important secular equations (Wilson *et al* 1955) in the theory of molecular vibrations are

$$\det |GF - \lambda E| = 0, \quad \text{or} \quad (GF)L = LA. \quad (1)$$

In a second order secular equation, we have two eigenvalues λ_i and λ_j and the elements of F and G matrices are related to them by the following equations:

$$G_{ii} F_{ii} + 2G_{ij} F_{ij} + G_{jj} F_{jj} = \lambda_i + \lambda_j \quad (2)$$

$$(G_{ii} G_{jj} - G_{ij}^2) (F_{ii} F_{jj} - F_{ij}^2) = \lambda_i \cdot \lambda_j. \quad (3)$$

Arranging and rewriting eq. (3), we have

$$[G_{ii} F_{ii} - (G_{ii} F_{ij}^2 / F_{jj})] [(F_{jj} \det G) / G_{ii}] = \lambda_i \cdot \lambda_j. \quad (4)$$

Neglecting the square of the L_{ij} term in eq. (1), it may be easily seen that $F_{jj} \det G / G_{ii} = \lambda_j$. Therefore eq. (4) can be split in two parts:

$$\lambda_i = G_{ii} F_{ii} - \alpha \quad \text{and} \quad \lambda_j = G_{jj} F_{jj} - \beta \quad (5)$$

where

$$\alpha = G_{ii} F_{ij}^2 / F_{jj} \quad \text{and} \quad \beta = G_{ij}^2 F_{jj} / G_{ii}. \quad (6)$$

From eqs (2) and (5), we get

$$2G_{ij} F_{ij} = -(\alpha + \beta) \quad (7)$$

and from eq. (6)

$$G_{ij}^2 F_{ij}^2 = \alpha \cdot \beta. \quad (8)$$

Equations (7) and (8) lead to the relation $\alpha = \beta$ which gives eqs (5) and (7) as:

$$G_{ii}F_{ii} = \lambda_i + \alpha \quad (9a)$$

$$G_{jj}F_{jj} = \lambda_j + \alpha \quad (9b)$$

$$G_{ij}F_{ij} = -\alpha \quad (9c)$$

Neglecting the square of the F_{ij} term in eq. (3) and substituting values of F_{ii} , F_{jj} from eq. (9) in eq. (3), we have

$$\alpha^2 + (\lambda_i + \lambda_j)\alpha - \lambda_i \lambda_j G_{ij}^2 / \det G = 0. \quad (10)$$

Now, on fixing the value of principal symmetrized force constant F_{ii} by eqs (9a) and (10), the remaining force constants, *i.e.*, F_{ij} and F_{jj} can be easily evaluated by eqs (2) and (3). It is to be noted here that eq. (10), being quadratic in α , has two roots. The positive root of α is chosen (Pandey *et al* 1976).

3. Results and discussion

The molecular data for thallos halide dimers, *e.g.*, Tl_2F_2 and Tl_2Cl_2 are given in table 1. The force constants evaluated in the present study are listed in table 2. It is noted from table 2 that the symmetrized force constants evaluated utilizing experimental mean amplitude $U_{T1 \dots T1}$ for Tl_2F_2 are in excellent agreement with those calculated by L-F approximation method. This shows the validity of L-F approximation in fixing the force field for Tl_2F_2 . The symmetrized force constants for Tl_2Cl_2 have also been evaluated by L-F approximation method and are listed in table 2.

The internal force constants for Tl_2F_2 and Tl_2Cl_2 evaluated by L-F approximation method are given in table 2. The results of the present study have been compared with those obtained by Lesiecki and Nibler (1975) by setting the stretch-stretch interaction constant f''_{rr} to zero (since it involves bonds on opposite sides of the ring and these have no common atoms). It is found that the stretching force constant f_r evaluated by these two methods are well comparable. It is important to note that the computed force constants (table 2) exhibit the expected trend of variation (Lesiecki and Nibler 1975).

In order to test the validity of the L-F approximation method in fixing the force field, the bond mean amplitude for Tl_2F_2 , *e.g.*, U_{T1-r} has also been evaluated utilizing the force field determined by L-F approximation method. This comes out

Table 1. Molecular data for Tl_2X_2 *

	Fundamental frequencies (cm^{-1})		Mean amplitudes (\AA) Tl_2F_2
	Tl_2F_2	Tl_2Cl_2	
$\nu_1 (A_g)$	226.0	131	
$\nu_2 (A_g)$	85.0	61	
$\nu_3 (B_{1g})$	297.0	190.4	$U_{T1 \dots T1} = 0.14 \pm 0.01$
$\nu_4 (B_{1u})$	81	..	$U_{T1-r} = 0.095 \pm 0.015$
$\nu_5 (B_{2u})$	316.0	189.6	
$\nu_6 (B_{3u})$	257.5	170.6	

* Lesiecki and Nibler (1975).

Table 2. Force constants* (M dyn/Å) for Tl_2X_2 molecules

F_{11}	Symmetrized force constants						Method
	F_{12}	F_{22}	F_{33}	F_{44}	F_{55}	F_{66}	
Tl_2F_2							
0.705	-0.085	0.508	0.727	0.134	0.791	0.959	L-F Approx.
0.709	-0.096	0.508	0.727	0.134	0.791	0.959	Mean amplitude
Tl_2Cl_2							
0.338	-0.056	0.270	0.594	..	0.572	0.572	L-F Approx.
f_r	Internal force constants						Method
	f_{rr}	f'_{rr}	f''_{rr}	f_R	f_{OP}	f_{RB}	
Tl_2F_2							
0.80	-0.05	0.04	-0.08	0.50	0.13	-0.04	L-F Approx.
0.87	0.03	0.11	0.0	0.80	0.13	-0.31	$f''_{rr} = 0$
Tl_2Cl_2							
0.52	-0.06	-0.06	-0.05	0.27	..	-0.03	L-F Approx.
0.57	-0.01	-0.003	0.0	0.39	..	-0.18	$f''_{rr} = 0$

* f_{rr} is an interaction through a common Tl atom, f'_{rr} an interaction through a common X-atom, and f''_{rr} an interaction between opposite sides of the ring.

to be equal to 0.11 \AA , while the experimental value reported by Solomonik *et al* (1974) is $0.095 \pm 0.015 \text{ \AA}$. A comparison of the two values shows that the mean amplitude, evaluated for Tl_2F_2 , is in reasonable agreement with the experimental value. For Tl_2Cl_2 , the mean amplitudes, evaluated in the present work, are $U_{Tl-Cl} = 0.14 \text{ \AA}$ and $U_{Tl \dots Tl} = 0.19_4 \text{ \AA}$ but unfortunately experimental value is not available for comparison. A higher mean amplitude is expected in Tl_2Cl_2 than in Tl_2F_2 since the bonds are much weaker in Tl_2Cl_2 .

It is concluded from the above discussion that the non-bond experimental mean amplitude $U_{Tl \dots Tl}$ for Tl_2F_2 is capable for fixing the force field and the L-F approximation method gives reasonably good force fields for these two thalious halide dimers, *e.g.*, Tl_2F_2 and Tl_2Cl_2 .

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