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STRUCTURAL AND THERMODYNAMIC ASPECTS OF AN ELECTRON-DIFFRACTION STUDY ON SATURATED THALLIUM MONOFLUORIDE VAPOR

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A fresh analysis has been performed on the original electron-diffraction data for saturated thallium monofluoride vapor. The diffraction data have been combined with spectroscopic ones to derive the equilibrium geometry and the complete harmonic force field in mdyn/Å for Tl_2F_2: $r_e(Tl-F) = 2.264(10)$ Å, $\angle FTlF = 73(1)°$, $F_1(A_g) = 0.67(13)$, $F_{12}(A_g) = -0.05(3)$, $F_2(A_g) = 0.15(2)$, $F_3(B_{1g}) = 0.93(13)$, $F_4(B_{1u}) = 0.041$, $F_5(B_{2u}) = 1.122$, $F_6(B_{3u}) = 0.893$, which gives the vibrational frequencies $\nu_1(A_g) = 263(15)$ cm^{-1}, $\nu_2(A_g) = 90(5)$ and $\nu_3(B_{1g}) = 334(20)$ cm^{-1}; formulas are given for the perpendicular mean-square vibration amplitudes and the transverse ones for cyclic X_2Y_2 molecules having D_{2h} symmetry. The saturated vapor at 700 K consists of monomers (51^{+7}_{-12} mole %) and dimers (49^{+12}_{-7}). The reaction $Tl_2F_2(g) \rightleftarrows 2TlF(g)$ has $\Delta_r H^0(298.15) = 134.7(3.4)$ kJ/mole and $\Delta_r S^0(298.15) = 134.69$ J/mole·K.

The structure of the Tl_2F_2 molecule has been discussed repeatedly. A linear structure has been derived from the early mass spectrometry and vapor-pressure measurements [1-3] and from spectroscopy [4]. A linear structure was also derived from an interpretation of the photoelectron spectra for the vapor [5], which was erroneously identified with thallium fluoride vapor.

When thallium fluoride vapor is used with electron diffraction, it is found that there are monomers and dimers, and it has been shown that Tl_2F_2 has a rhombic planar or near-planar structure [6, 7]. A thallium fluoride molecular beam in an inhomogeneous electric field [8] showed behavior in agreement with the electron-diffraction conclusions [6, 7]. Slow-electron scattering by a thallium monofluoride vapor jet cannot be interpreted satisfactorily on the assumption that the dimer has a linear structure [9].

Later, during a repeat examination of thallium fluoride vapor photoelectron spectra, it was confirmed [10] that a planar rhombic structure applies for Tl_2F_2. The infrared and Raman structures recorded in [11] also indicate a cyclic structure for Tl_2F_2, D_{2h} symmetry. In calculations from an ionic model containing polarizable ions [12, 13], it was shown that a planar rhombic structure for Tl_2F_2 is preferable to a linear one.

Tl_2F_2 with D_{2h} symmetry has six normal vibrations, three of which ($2A_g B_{1g}$) are active in Raman scattering and three (B_{1u}, B_{2u}, B_{3u}) in the infrared. In [11], the Raman and IR

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TABLE 1. Effective Tl_2F_2 Configuration Parameters (T = 700 ± 50 K)

Param-eter	(Tl—F)	(Tl—Tl)	(F—F)
r_g, Å	2,302(9)*	3,668(9)	2,67(13)
l, Å	0,107(10)	0,137(5)	0,12(8)

*The total errors are given in parentheses:

$\sigma = [\sigma^2_{sc} + (2.5\sigma_{LS})^2]^{1/2}$ for the distances

and $\sigma = 2.5\sigma_{LS}$ for the amplitudes.

spectra were recorded for thallium fluoride molecules isolated in an argon matrix, which indicated that monomers and polymers occur. All six normal vibrations were identified for Tl_2F_2, and assignments were made to symmetry types. An attempt was made to use preliminary electron-diffraction data [6] to determine the force field, but this did not narrow the permissible range for the nondiagonal force constant in the block A_g on account of inaccuracy in the vibration amplitudes, and also because of error in the expression for the element G_2 of the kinematic-coefficient matrix. In [4], two frequencies were recorded for Tl_2F_2 (argon matrix, infrared), which coincided numerically with the values measured under analogous conditions in [11] but which had been erroneously assigned to a linear structure.

The Tl_2F_2 frequencies were calculated in [12, 13] from an ionic model containing polarizable ions, but there were large differences in some of the frequencies from the measured [11] ones.

In [14], correct expressions were used for the elements of the G matrix for an M_2X_2 molecule having D_{2h} symmetry, in contrast to [11], and the [4] frequencies were used with the preliminary electron-diffraction data [6] to determine the Tl_2F_2 frequencies inactive in the IR. ALthough a simplified force field was used [14], the calculated deformation frequency and one of the stretching frequencies agreed well with direct measurements [11].

The exact composition for saturated thallium fluoride vapor has been determined by various methods over the solid and liquid phases [1-3, 15]; the data are not directly comparable because they relate to differing conditions. Attempts to convert them to a single temperature result in a spread in the monomer-dimer ratio of almost an order of magnitude.

There is satisfactory agreement between the enthalpy and entropy of dimerization for thallium monofluoride given in [15, 16] and derived from the third law of thermodynamics. Much worse results are obtained from the second law [2, 15] and the ionic model [13].

Here we consider research on thallium fluoride vapor by electron diffraction [6, 7], where we deal with the equilibrium configuration, the revised force field for Tl_2F_2, and the composition of the vapor over TlF, as well as the enthalpy and entropy of $Tl_2F_2 \rightleftarrows 2TlF$ derived from the electron diffraction data.

STRUCTURAL ANALYSIS IN TERMS OF
EFFECTIVE MOLECULAR PARAMETERS

We used the [6, 7] original measurements. The reduced molecular scattering intensity function $sM_{exp}(s)$ was corrected on the basis of the trend in the low-frequency component of the difference $\Delta sM(s) = sM_{exp}(s) - h \cdot sM_{th}(s)$, where h is a normalization coefficient. The final structure-parameter and composition refinement was based on the combined $sM_{exp}(s)$ composed on the basis of the scales for the individual segments corresponding to two different distances from the nozzle to the photographic plate. A difference from [6, 7] was that at all stages in the structure analysis we varied the internuclear distance r_a(F—F) without reference to the other parameters, while in refining the mean l(F—F) vibration amplitude at each step in the least squares analysis, we used increments equal to those in l(Tl—Tl), and in the final stage, l(F—F) was also varied independently. Figure 1 reflects the procedure for refining the proportions of monomer and dimer in the vapor. When the vapor composition and Tl_2F_2 parameters were refined, we derived those for TlF from spectral data [17, 18]. The monomer and dimer contents were 51^{+7}_{-12} and 49^{+12}_{-7} mole % correspondingly. The errors have been derived by the [19] method and correspond to the 95% confidence limits.
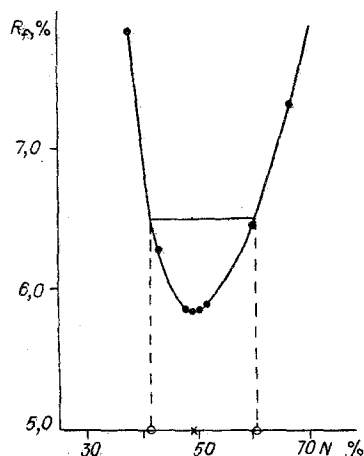
Fig. 1. Variation in the discrepancy factor between the experimental and theoretical sM(s) curves on varying the vapor composition.

TABLE 2. Perpendicular and Transverse Mean-Square Vibration Amplitudes for M_2X_2, Symmetry D_{2h}

Distance type	
M—X	$\langle \Delta x^2 \rangle = \dfrac{1}{8}\,\Sigma_{22}\,(A_g) + \dfrac{1}{16}\left[\dfrac{m_M - m_X}{D}\sin 2A\right]^2 \Sigma\,(B_{1g}) +$ $\dfrac{1}{4}\,\mathrm{ctg}^2\,A\Sigma\,(B_{2u}) + \dfrac{1}{4}\,\mathrm{tg}^2\,A\Sigma\,(B_{3u})$ $\langle \Delta y^2 \rangle = \dfrac{1}{4}\,\Sigma\,(Bg_{1u})$ $\langle \Delta x \cdot \Delta y \rangle = -\dfrac{1}{4\sqrt{2}}\,\Sigma_{12}\,(A_g) + \dfrac{1}{8}\,\dfrac{m_M - m_X}{D}\sin 2A\Sigma\,(B_{1g}) -$ $\dfrac{1}{4}\,\mathrm{ctg}\,A\Sigma\,(B_{2u}) + \dfrac{1}{4}\,\mathrm{tg}\,A\Sigma\,(B_{3u})$
X—X	$\langle \Delta x^2 \rangle = \left[-\dfrac{m_M \cos A}{D}\right]^2 \Sigma\,(B_{1g})$
M—M	$\langle \Delta x^2 \rangle = \left[-\dfrac{m_X \sin A}{D}\right]^2 \Sigma\,(B_{1g})$

Note: $D = m_X\sin^2 A + m_M\cos^2 A$, $2A = \angle X - M - X$,

Table 1 gives the parameters of the effective r_g configuration for Tl_2F_2 calculated from the least-squares analysis for sM(s) for the optimum vapor composition. The major parameters agree with those in [6, 7] and confirm a planar rhombic structure for Tl_2F_2.

STRUCTURE ANALYSIS IN TERMS OF THE Tl_2F_2 POTENTIAL-FUNCTION PARAMETERS

The parameters for Tl_2F_2 found from the traditional approach in the previous stage in essence are not molecular constants because they are dependent on temperature. One can transform from the effective r_g parameters to the equilibrium r_e ones if the force field is known. Harmonic and anharmonic effects can be incorporated sequentially.

The complete harmonic force field for an M_2X_2 molecule having D_{2h} symmetry in the symmetry coordinates* contains, in accordance with the vibrational representation $\Gamma = 2A_g + B_{1g} + B_{1u} +$

*The symbols for the vibration types are dependent on the coordinate system and can be compared for the different sources as follows:

$A_g \quad B_{3g} \quad B_{1u} \quad B_{2u} \quad B_{3u}$ [14, 20];

$A_g \quad B_{1g} \quad B_{2u} \quad B_{3u} \quad B_{1u}$ [11, 21—23];

$A_g \quad B_{1g} \quad B_{3u} \quad B_{2u} \quad B_{1u}$ [This paper]

TABLE 3. Tl_2F_2 Force Field (mdyn/Å)

F_{ij}	[11]	[14]*	Our data
$F_1(A_g)$	1,021(50)	0,71(3)	0,67(13)
$F_{12}(A_g)$	—0,632(32)	0	—0,05(3)
$F_2(A_g)$	0,8040(2)	0,13(4)	0,15(2)
$F_3(B_{1g})$	0,728	0,71(3)	0,93(13)
$F_4(B_{1u})$	0,135	—	[0,041] †
$F_5(B_{2u})$	0,793 ‡	0,93(4)	[1,122] ·†
$F_6(B_{3u})$	0,956 ‡	0,79(4)	[0,893] †

*F_{ij} calculated from the force constants in the
internal coordinates via the [14] formulas.
†Calculated from the vibration frequencies and
not varied during the structure analysis.
‡These quantities should be interchanged in
accordance with the incorrect assignment of the
force-constant equations in the symmetry coordi-
nates and the internal coordinates for the B_{2u}
and B_{3u} vibration types [11].

$B_{2u} + B_{3u}$, seven constants: $F_1(A_g)$, $F_{12}(A_g)$, $F_2(A_g)$, $F_3(B_{1g})$, $F_4(B_{1u})$, $F_5(B_{2u})$, $F_6(B_{3u})$, so six vibrational frequencies are insufficient to define it. In that case, one usually employs additional information on the Coriolis constants or isotopic shifts, but there is little prospect of determining them for this species.

In [11, 14], the Tl_2F_2 force field was calculated by combining electron-diffraction and spectroscopic data, but the former were from a preliminary experiment [6], while in [11], erroneous formulas were used for the matrix elements G_{22}, G_{12}, and G_{44}, while in [14], only two measured frequencies [4] were used with a simplified model.

One can determine the equilibrium parameters and force field by the [24] method, in which $sM(s)$ can be parameterized from the force constants F_{ij} and the internuclear distances r_e^h at equilibrium in the harmonic approximation. The method requires one to have formulas relating the generalized vibration amplitudes to the force field.

In [14], the in-plane vibrations for Tl_2F_2 were considered and expressions were derived for the kinematic-coefficient matrix elements G_{ij} and the parallel mean-square vibration amplitudes ℓ_{ij}^2. In [23], formulas are given for the G_{ij}, which include an element for out-of-plane vibration, for M_2X_2. As no formulas for the perpendicular and transverse mean-square amplitudes are given in the literature, we give them in Table 2.

According to Table 1, the parameters for the (F-F) term have been determined unreliably, so the main contribution to $sM(s)$ comes from the four vibrational parameters $\langle\Delta z^2\rangle_{Tl-F}$, $\langle\Delta z^2\rangle_{Tl-Tl}$, $u_{Tl-F} = \langle\Delta x^2\rangle_{Tl-F} + \langle\Delta y^2\rangle_{Tl-F}$, $u_{Tl-Tl} = \langle\Delta x^2\rangle_{Tl-Tl} + \langle\Delta y^2\rangle_{Tl-Tl}$, and correspondingly, one can derive not more than four force constants from $sM(s)$ analysis.

One can determine r_e^h, the F-Tl-F angle, and the total force field by supplementing the electron-diffraction data with the $\nu_4(B_{1u})$, $\nu_5(B_{2u})$ and $\nu_6(B_{3u})$ vibrational frequencies corrected for the matrix shift in accordance with the Na_2F_2 spectrum [25, 26]. Here we assumed that the resulting force field would enable one to assign the bands peaking at 226 and 297 cm^{-1} [11], as the assignment has been criticized in [13].

Table 3 gives the Tl_2F_2 force field derived from a least-squares analysis of the electron-diffraction and spectral data together with the force constants found in [11, 14]. The ratio of monomer and dimers is an independent parameter here. We found that the two were present in almost equal amounts under our conditions $N_{mon}/N_{dim} = (0.46 \pm 0.04)/(0.54 \pm 0.04)$. The F-Tl-F bond angle is $73 \pm 1°$.

TABLE 4. Normal Vibration Frequencies (cm^{-1}) for Tl_2F_2

$\nu_1(A_g)$	$\nu_2(A_g)$	$\nu_3(B_{1g})$	$\nu_4(B_{1u})$	$\nu_5(B_{2u})$	$\nu_6(B_{3u})$	Method, Ref.
226	93	297	81	257,5 •	316	IR, Raman, argon matrix [11]
352	108	235	82	303	360	Calculation, ionic model [13]
263(15)	90(5)	334(20)	[90] *	[278] *	[336] *	Our data

*Values from [11] used, corrected for matrix shift.

TABLE 5. Thermodynamic Characteristics
for the $Tl_2F_2 \rightleftarrows 2TlF$ Vapor-State Reaction

$\Delta_r H^0(298,15)$, kJ/mole	$\Delta_r S^0(298,15)$, J/mole·K	Source
130,98±5	133,08	[15]
141±4	131,07	[16]
134,8±3,4	134,69	Our data

DISCUSSION

Structure

The electron-diffraction, spectroscopic [4, 11], and thermodynamic [15] data together indicate a planar rhombic structure for Tl_2F_2.

Our $r_e^h(Tl-F)$ result is an estimate of the equilibrium $r_e(Tl-F)$ because the harmonic approximation was used. One can estimate the anharmonic contribution to $r_e^h(Tl-F)$ by the [27] method. That crude approach has been shown [28] to give acceptable results for polyatomic molecules if there is a specific correlation between the dynamic and kinematic anharmonicities. The $r_e(Tl-F)$ obtained in that scheme is 2.264 ± 0.010 Å. According to [29], those anharmonicities for out-of-plane vibrations for Tl_2F_2 are small, so we recommend 73 ± 1°, which is derived from the potential method, as an estimate of the equilibrium F–Tl–F angle.

Force Field and Vibration Frequencies

Our complete force field in the harmonic approximation is compared in Table 3 with the [11, 14] one. The reasons for the marked differences in the corresponding force constants have been discussed above.

An interesting point concerns the assignment of the A_g and B_{1g} stretching frequencies. It was assumed that $\nu_1(A_g) < \nu_3(B_{1g})$ in the spectral study [11], but in [13, 30], calculations from the ionic model led to the opposite conclusion. A least-squares analysis of the electron-diffraction data supplemented with the measured [11] $\nu_4(B_{1u})$, $\nu_5(B_{2u})$, $\nu_6(B_{3u})$ frequencies leads to a relation between the force constants that confirms the [11] assignment. The resulting vibration frequencies are given in Table 4. The values found for $\nu_1(A_g)$ and $\nu_3(B_{1g})$ exceed those measured in [11], which is natural because the interaction with an inert-gas matrix usually reduces the vibration frequencies.

For $\nu_2(A_g)$, in [11] the value measured in the matrix is given, which is higher than that found here, which raises the question of whether the assignment to $\nu_2(A_g)$ in [11] for the band having wave number 93 cm^{-1} is correct instead of the simultaneously recorded 85 cm^{-1}, which has almost the same intensity.

Vapor Composition and Thermodynamics

We have used electron diffraction not only as a structural tool but also as an analytical one for determining the proportions of monomer and dimer. The molar fraction of dimer at 700

K was 49^{+12}_{-7} which agrees well with the values calculated from pressure measurements [15], 42 ± 20, and mass spectrometry [2], (72^{+21}_{-16}), as well as that obtained from a repeat analysis of the measurements in [7]: 52 ± 8.

We used these concentrations with the Tl_2F_2 structure parameters and with the [11] frequencies corrected for the matrix shift to calculate the dimerization enthalpy and entropy. The saturation vapor pressure* needed to convert the equilibrium constant K_x to the constant K_p was taken from [31]. Table 5 compares the values with published ones. The agreement over $\Delta_r H^0(298.15)$ found in [15] and here indicates that the characteristic is determined reliably and enables one to refine the [16] enthalpy of formation for gaseous thallium monofluoride. As $\Delta_f H^0(0)(TlF) = -183.946 \pm 3.4$ kJ/mole [16], $\Delta_f H^0(0) (Tl_2F_2) = -502.6 \pm 8.1$ kJ/mole. The recommended values for the dimerization enthalpy and entropy are: $\Delta_r H^0(298.15) = -133.8 \pm 4.3$ kJ/mole and $\Delta_r S^0(298.15) = -133.58$ J/mole·K, which are derived by averaging the [15] values and ours.

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*The vapor pressure has been calculated without correction for the error in measuring the temperature in the electron-diffraction experiment.