



Equilibrium Structure of Monomeric GaCl₃ and InCl₃ from Combined Analysis of Gas Electron Diffraction and Vibrational Spectroscopic Data

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The equilibrium structures of monomeric gallium and indium trichloride have been determined in harmonic approximation by means of the combined analysis of gas electron diffraction intensities and vibrational frequencies. The molecules are planar and have $r_e^h(M-Cl)$ distances of 2.100(3) and 2.275(3) for GaCl₃ and InCl₃, respectively. Force constants are also obtained for both molecules. © 1994 Academic Press, Inc.

INTRODUCTION

The molecular structures of gaseous GaCl₃ and InCl₃ have been determined independently in two different groups by Girichev *et al.* (1) and Haaland *et al.* (2). Table I, which summarizes their results, indicates that the traditional electron diffraction parameters (thermal average internuclear distances and mean amplitudes of vibration) may increase with increasing temperature. This enhancement may exceed the experimental error limits. It renders the application of these data as molecular characteristics problematic. Therefore the presentation of the experimental electron diffraction data in form of potential function parameters is desirable.

In both studies (1, 2) the assignment of the molecular symmetry to the D_{3h} point group has been established for each of these molecules according to the agreement of the experimental shrinkage effect with the theoretical analogue, which has been calculated from the spectroscopic vibrational frequencies for a planar configuration using Cyvin's formalism (3).

The vibrational spectra are well known for GaCl₃ (4-9) and InCl₃ (4-6). From these data (4, 7-9) it was established that these molecules have a planar D_{3h} structure in the vapor. The obtained frequencies are listed in Tables II and III. The force constants for GaCl₃ (5, 9-11) and InCl₃ (2, 5), which reproduce the observed frequencies well, are also given in Tables II and III, respectively.

This work presents the determination of potential function parameters for GaCl₃ and InCl₃ directly from the experimental molecular intensity curves, which were recorded previously (2). The application of the harmonic approximation (12) seems to be useful in these cases, because the anharmonic parameters $\kappa(M-Cl)$ are small (2).

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TABLE I

Thermal Average Internuclear Distances (r_g) and Mean Amplitudes of Vibration (l) for Gallium and Indium Trichloride

Molecule	T/K	$r_g(\text{M-Cl})/\text{\AA}$	$l(\text{M-Cl})/\text{\AA}$	Ref.
GaCl ₃	322	2.097	0.047	1
	445	2.101	0.053(3)	1
	656	2.110(3)*	0.061(2)	2
InCl ₃	611	2.274(5)	0.068(3)	1
	753	2.291(5)*	0.070(6)	2
	883	2.289(5)	0.080(5)	1

* Calculated from the r_a value given in Ref. (2).

THEORY

The applied reduced intensity distribution of electron scattering has the form (12)

$$sM(s) = \sum_{i,j}^n g_{ij}(s)(r_{e,ij}^h)^{-1} \exp[-s^2 \langle \Delta z_{ij}^2 \rangle / 2] \times [L_{ij}(s) \sin(sr_{e,ij}^h) + N_{ij}(s) \cos(sr_{e,ij}^h)], \quad (1)$$

TABLE II

Molecular Parameters for Gallium Trichloride in Harmonic Approximation

Parameter ^a	Joint analysis		III ^b	ED alone IV ^b	V ^b	Literature data		
	I ^b	II ^b						
r_e^h \AA	2.101(2)	2.100(3)	2.100	2.100	2.099			
f_r mdyn/\AA	2.65(18)	2.61(8)	2.58	2.61	2.77	2.785(22) ^c	2.63(1) ^d	2.71 ⁱ
f_{rr} mdyn/\AA	0.22(22)	0.14(22)	0.20 ^f	0.20 ^f	0.20 ^f	0.099(13) ^c	0.21(2) ^d	0.18 ⁱ
F_{11} mdyn/\AA	3.09(22)	2.89(22)	2.98	3.01	3.14	2.983 ^c		
F_{22} mdyn/\AA	0.06(9)	0.06(1)	0.06 ^g	0.06 ^g	0.06 ^g	0.055 ^{ch}	0.057(1) ^{dh}	
F_{33} mdyn/\AA	2.43(22)	2.47(22)	2.38	2.41	2.57	2.686 ^c		2.567 ⁱ
F_{34} mdyn/\AA	0.09(11)	-0.06(1)	0.0	-0.06	-0.14	-0.141(22) ^c		-0.063 ⁱ
F_{44} mdyn/\AA	0.10(2)	0.08(1)	0.084	0.079	0.076	0.084(2) ^{ch}	0.08(1) ^{dh}	0.082 ⁱ
$\nu_1(A_1')$ cm ⁻¹	384(15)	372(14)	378	379	389	382 ^j , 381 ^k , 383 ^{lm}		
$\nu_2(A_2'')$ cm ⁻¹	148(12)	150(13)	148	148	148	145 ⁿ , 136.2 ^{om} , 143 ^c		
$\nu_3(E')$ cm ⁻¹	471(20)	452(20)	453	447	451	450 ⁿ , 470 ^{om} , 457 ^k , 467 ^{lm} , 464 ^c		
$\nu_4(E')$ cm ⁻¹	133(14)	128(8)	130	127	123	128 ^{ka} , 132.1 ^{om} , 132 ^{lm} , 131 ^c		
ζ_s	0.61	0.43	0.51	0.43	0.33	0.4320 ^p , 0.43(2) ^r		
R(50) %	2.6	2.6	2.6	2.7	2.8			
R(25) %	5.0	5.1	5.1	5.1	5.1			

^a Uncertainties parenthesized in units of the last significant figures; for r_e^h estimated according to Ref. (2); $2\sigma_{LS}$ for force constants and for frequencies derived from uncertainties of force constants.

^b Different approximations or assumptions for F_{34} : (I) based on the exact solution of the second-order secular equation for the E' -type vibrations, (II, IV) based on the Larnaudie approximation for the solution of the secular equation, (III) $F_{34} = 0$, and (V) value from Ref. (9).

^c Ref. (9). ^d Ref. (10). ^e Ref. (7).

^f Fixed at value of joint analysis and literature (see text).

^g Fixed (see text).

^h Modified value.

ⁱ Ref. (11). ^j Ref. (4). ^k Ref. (8). ^l Ref. (5).

^m Superscript m labels frequencies in the matrix, whereas all other frequencies are in the gas phase.

ⁿ Ref. (6). ^o Ref. (17). ^p Ref. (18).

TABLE III

Molecular Parameters for Indium Trichloride in Harmonic Approximation

Parameter ^a	Joint analysis ^b	ED alone ^b	Literature
r_e^h Å	2.275(3)	2.275	
f_r mdyn/Å	2.20(16)	2.12	2.38 ^c
f_{rr} mdyn/Å	0.13(23)	0.13 ^d	0.14 ^c
F_{11} mdyn/Å	2.46(23)	2.38	2.56 ^e
F_{22} mdyn/Å	0.044(10)	0.044 ^f	0.06 ^{e,g}
F_{33} mdyn/Å	2.07(23)	1.99	2.39 ^e
F_{34} mdyn/Å	-0.03(1)	-0.03	
F_{44} mdyn/Å	0.050(6)	0.051	0.052 ^{e,g}
$\nu_1(A_1')$ cm ⁻¹	344(16)	338	350 ^{h,i} 356 ^{c,k}
$\nu_2(A_2'')$ cm ⁻¹	110(13)	110	110 ^{h,i}
$\nu_3(E')$ cm ⁻¹	379(16)	372	400 ^{c,k}
$\nu_4(E')$ cm ⁻¹	100(6)	98	94 ^{h,i} 95 ^{h,i} 119 ^{c,k}
ζ_3	0.31	0.31	0.30(5) ^l
R(50) %	6.1	6.1	
R(25) %	14.1	14.2	

^a) see footnote a in Table II ^b) based on Larnaudie approximation for the E'-type vibrations ^c) Ref. 5 ^d) fixed at value of joint analysis (see text)
^e) Ref. 2 ^f) fixed value (see text) ^g) modified value ^h) Ref. 4 ⁱ) gas phase
^j) Ref. 6 ^k) argon matrix isolation ^l) Ref. 18

with (omitting the subscripts ij)

$$L(s) = 1 + \langle \Delta z^2 \rangle / (r_e^h)^2 - u/2(r_e^h)^2 - s^2[\langle \Delta z^2 \rangle / (r_e^h)^2 - v/2(r_e^h)^2]$$

$$N(s) = -s[\langle \Delta z^2 \rangle / r_e^h - u/2r_e^h + s^2v/2r_e^h]$$

$$u = \langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle$$

$$v = \langle \Delta x \Delta z \rangle^2 + \langle \Delta y \Delta z \rangle^2,$$

where n is the number of nuclei in the molecule, g the scattering function, s the standard scattering variable, r_e^h the harmonic equilibrium distance, and Δz the parallel and Δx and Δy the perpendicular displacements of the atom pairs, respectively.

The generalized mean square amplitudes of vibration $\langle \Delta x^2 \rangle_{ij}$, $\langle \Delta y^2 \rangle_{ij}$, $\langle \Delta z^2 \rangle_{ij}$, $\langle \Delta x \Delta z \rangle_{ij}$, and $\langle \Delta y \Delta z \rangle_{ij}$ (13) are related to the force constants by the familiar relationship given, e.g., in Refs. (13, 3). For planar MX_3 molecules only four amplitude parameters are different from zero, viz. $\langle \Delta z^2 \rangle_{MX}$, $\langle \Delta z^2 \rangle_{XX}$, u_{MX} , and u_{XX} .

However, the general force field of planar MX_3 molecules is defined by five force constants in the linearized symmetry coordinates (3): $F_{11}(A_1')$, $F_{22}(A_2'')$, $F_{33}(E')$, $F_{34}(E')$, and $F_{44}(E')$. In order to solve this underdetermined inverse problem it is necessary to use additional information. The joint analysis of electron diffraction (ED) and spectroscopic data (SP), proposed by Spiridonov *et al.* (12), solves this problem by limiting the range of allowed force constant values by means of restricted frequency intervals, which are adjusted by the mean of the weighting factors. Such a regularization method of the underdetermined inverse vibrational problem stabilizes the solutions in the mathematical sense; however, the physical definiteness of some "weak" param-

eters can be overemphasized because of the insufficient information content of the experimental intensity curve relative to these parameters.

The solution of the inverse vibrational problem on the basis of electron diffraction intensities alone can be performed under certain assumptions for the nondiagonal matrix element F_{34} , e.g.; (1) in Larnaudie's approximation (14), $F_{34} = -F_{44} \cdot G_{34} / G_{33}$, where G_{ij} are matrix elements of the kinematic coefficients, and (2) $F_{34} = 0$, or estimated from literature data.

The optimized function has been expressed as

$$G = \sum_k^L p_k (y_k^{\text{exp}} - y_k^{\text{calc}})^2, \quad (2)$$

where y_k^{exp} and y_k^{calc} are the manifolds of observed quantities and of corresponding calculated analogues, L the total number of quantities being compared, and p_k the weighting coefficients, which is inversely proportional to the squared deviations of the quantities. The function G has been minimized by Hooke and Jeeves' random search method (15). The applied FORTRAN program POTENXY3 was developed by A. G. Gershikov and slightly modified by N. Vogt for the present work.

STRUCTURAL AND VIBRATIONAL ANALYSIS OF EXPERIMENTAL DATA

Gallium Trichloride

Under the conditions of the electron diffraction experiment (2) about 9% GaCl was observed besides GaCl₃. Therefore the contribution by the monochloride has been subtracted from the scattering intensities $I_{\text{mol}}(s)$. Thus the R -factors in the traditional analysis have been slightly increased in comparison with the original analysis (2) to $R(50) = 2.4\%$ and $R(25) = 5.0\%$.

Because F_{11} strongly correlates with F_{33} , these force constants have been determined by optimizing the valence force constants f_r (Ga-Cl stretch) and f_{rr} (the interaction between the Ga-Cl stretching motion), which are related in the following way (e.g., Ref. 3):

$$F_{11} = f_r + 2f_{rr} \quad (3)$$

$$F_{33} = f_r - f_{rr}. \quad (4)$$

During the optimization of the G criterion a deviation of 5% has been permitted for each quantity $y_k(I_{\text{mol}}(s), \nu_1, \nu_2, \nu_3, \text{ and } \nu_4)$. The molecular intensity curve, obtained with a nozzle-to-plate distance of 25 cm, also has the relative weight of 0.5 in comparison with the curve for the 50-cm distance (2). The results of the combined analysis of gas electron diffraction intensities (2) and spectroscopic frequencies ($\nu_1(4)$, ν_2, ν_3 , and $\nu_4(9)$) are given in Table II.

The analysis of the ED data alone has been performed under some assumptions. Preliminary calculations have shown that the doubling of the F_{22} constant changes the total R -factor by only 0.05%. That means that the optimization criterion is insensitive to this parameter. Thus F_{22} has been constrained to a value, which has been obtained in the joint analysis (ED + SP) and which agrees well with literature. The results are summarized in Table II. It also contains values for the Coriolis coupling constant ζ_3 , which has been calculated by means of Cyvin's formula (16),

$$\zeta_3 = \{3\mu_X(\lambda_3 + \lambda_4) + 48^{1/2}F_{34}\mu_Y(3\mu_X + \mu_Y)\}/(\lambda_3 - \lambda_4)(3\mu_X + 2\mu_Y), \quad (5)$$

where λ_i are the familiar frequency parameters (proportional to the squared wave-numbers), whereas μ_X and μ_Y are the inverse masses of the Ga and Cl atoms, respectively.

As seen in Table II the R_f values do not change significantly at the variation of F_{34} in the interval 0.09 to -0.14 mdyn/Å. However, only the value $F_{34} = -0.06$ mdyn/Å yields a ζ_3 value, which agrees best with the calculated data from literature (11, 17, 18). Therefore the Larnaudie approximation for E' -type vibrations should be preferred and the parameter set in column II is recommended. In the general case, if spectroscopic data are unavailable, the vibrational analysis on the basis of electron diffraction data alone may be possible if "weak" parameters, which have little effect on the calculated intensity curve, are estimated correctly. As expected the resulting $r_e^h = 2.100(3)$ Å is numerically consistent with r_α (19) of $2.098(3)$ Å, which may be derived from the data given in Ref. (2).

The obtained values of force constants, vibrational frequencies, and Coriolis coupling constant agree well with the literature values. The good agreement of the R -factors with those of the traditional GED analysis shows that the harmonic approximation of the potential function is sufficient.

The joint analysis of ED and SP data in terms of a pyramidal model yields $\langle \nu_e^h(\text{ClGaCl})$ bond angle of $119.7(5)^\circ$. This verifies the trigonal planar equilibrium configuration in agreement with the previous studies (1, 2).

Indium Trichloride

According to the data (2) InCl₃ was a component of a mixture with 59 mol% InCl. Therefore in comparison with the original analysis (2) the R -factors have been significantly enlarged due to the subtraction of the contribution of the monochloride from the scattering intensities ($R(50) = 6.1\%$, $R(25) = 14.3\%$, and $R_{\text{total}} = 7.8\%$). The weight factor for the ED data in the joint analysis has been calculated on the basis that the accuracy of the determination $I_{\text{mol}}(s)$ is about 8%.

Moreover, the molecular intensity curve, obtained with a nozzle-to-plate distance of 25 cm, also has the relative weight of 0.4 in comparison with the curve for the 50-cm distance (2). All other details of the analysis correspond with those for GaCl₃. The results for the joint analysis of electron diffraction intensities (2) and vibrational frequencies (ν_1 and $\nu_4(4)$, $\nu_2(6)$, $\nu_3(5)$) and the ED data alone in Larnaudie approximation for the E' -type vibrations as well as the calculated ζ_3 values are listed in Table III. In conclusion the parameter set in column I is recommended.

The $r_e^h = 2.275(3)$ Å is numerically consistent with $r_\alpha = 2.272(5)$ Å, which can be derived from previous data (2). Again, the obtained values of force constants, vibrational frequencies, and Coriolis coupling constant agree well with the literature values.

The analysis of experimental data (ED + SP) in terms of a pyramidal model leads to an $\langle \nu_e^h(\text{ClInCl})$ bond angle of $119.4(7)^\circ$, which unambiguously supports the trigonal planar equilibrium configuration established previously.

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