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# The molecular structure of $\text{ScI}_3$ and $\text{Sc}_2\text{I}_6$ determined by gas-phase electron diffraction and theoretical studies

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## Abstract

The structure of the  $\text{ScI}_3$  molecule has been studied by synchronous gas-phase electron diffraction and mass spectrometric experiment combined with theoretical studies. The saturated vapour over  $\text{ScI}_3$  at 896(10) K contained  $\sim 96$  and 4 mol% of monomeric and dimeric species, respectively. The following structural parameters of  $\text{ScI}_3$  have been determined:  $r_g(\text{Sc}-\text{I})=2.650(5)$ ,  $r_g(\text{I}\cdots\text{I})=4.530(10)$  Å,  $\angle_g(\text{I}-\text{Sc}-\text{I})=117.6(4)^\circ$ . Quantum chemical investigation of  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules using DFT and MP2 approaches has been carried out. According to the results of both experimental and theoretical studies the equilibrium geometry of scandium triiodide molecule is planar ( $D_{3h}$  symmetry) and the  $\text{Sc}_2\text{I}_6$  molecule possesses a structure of  $D_{2h}$  symmetry with four Sc–I bridge bonds.  
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**Keywords:** Scandium triiodide; Scandium triiodide dimer; Molecular structure; Gas-phase electron diffraction; Mass spectrometry; Quantum chemical calculations; Ab initio calculations

## 1. Introduction

The molecular structure of monomeric scandium trihalides,  $\text{ScX}_3$ , was the subject of several investigations during the last 40 years. These studies have pursued two main goals: determining the Sc–X bond length values and answering the question about the symmetry of  $\text{ScX}_3$  equilibrium structure, which may be pyramidal ( $C_{3v}$ ) or planar ( $D_{3h}$ ).

The first investigation of  $\text{ScF}_3$  by gas-phase electron diffraction (GED) was carried out by Akishin and Naumov [1] in 1961. The molecule was found to possess  $D_{3h}$  symmetry. However, due to the simplified approach used for data analysis in [1] this conclusion was quite unreliable. The authors [1] recorded the diffraction pattern starting from  $s=4.0$  Å. Within the range of  $s=0\text{--}4$  Å the molecular intensity curve was expanded using the theoretical one calculated in the assumption that the molecule is planar. Moreover, the authors [1] have not taken into consideration

the shrinkage of  $\text{F}\cdots\text{F}$  distance and assumed  $r_g(\text{F}\cdots\text{F})=\sqrt{3}r_g(\text{Sc}-\text{F})$ .

Three works on the IR absorption spectra of  $\text{ScF}_3$  were performed in 1966–1975 [2–4]. Since the Sc–F symmetric stretching frequency ( $\nu_1$ ) was not detected in any of the experiments mentioned, it was concluded that the  $\text{ScF}_3$  molecule should be planar ( $D_{3h}$  symmetry) or very nearly so [4]. On the other hand, the investigation of electric deflection of molecular beams [5] indicated a polar (i.e. having a dipole moment) structure.

The second GED study [6] yielded a non-planar structure with a  $\angle_g(\text{F}-\text{Sc}-\text{F})$  valence angle of  $110(2.5)^\circ$ . Finally, the third GED investigation of  $\text{ScF}_3$  molecule [7] has given results consistent with the planar  $D_{3h}$  equilibrium structure. The two theoretical studies [8,9] also indicated  $D_{3h}$  equilibrium geometry of scandium trifluoride molecule.

The gas-phase IR absorption spectra of  $\text{ScCl}_3$ ,  $\text{ScBr}_3$ , and  $\text{ScI}_3$  were studied by Selivanov et al. [10]. Only one wide band was detected in each case, assigned by the authors [10] to the  $\nu_3$  vibrational frequencies of the corresponding molecules. No bands that could be assigned to  $\nu_1$  symmetric stretching frequencies were detected. The region below  $100\text{ cm}^{-1}$  (where  $\nu_2$  and  $\nu_4$  frequencies are expected) has

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not been studied. In the study [11], the IR absorption spectrum of  $\text{ScBr}_3$  had three bands assigned to  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  vibrational frequencies. The absence of a band that could be assigned to  $\nu_1$  frequency may provide evidence that the  $\text{ScBr}_3$  molecule has  $D_{3h}$  equilibrium symmetry, but the authors [11] stated that more thorough studies of IR and Raman spectra are required to answer this question.

Scandium trichloride was studied by gas-phase electron diffraction and quantum chemical calculations in 1998 [12]. The DFT calculations and experiment both agreed that the  $\text{ScCl}_3$  molecule is planar ( $D_{3h}$  symmetry). Moreover, CISD(Q) ab initio investigation [9] yielded  $D_{3h}$  equilibrium geometry for all scandium trihalide molecules. No GED data concerning the structure of scandium tribromide exists up to the present time.

The structure of scandium triiodide was studied by GED in 1995 by Ezhov et al. [13]. It was found that at 1050 K the vapour over  $\text{ScI}_3$  contained 75% of dimeric species and 25% of monomer. According to the results [13,14], the  $\text{ScI}_3$  molecule is planar ( $D_{3h}$  symmetry) and the  $\text{Sc}_2\text{I}_6$  molecule possesses a structure of  $D_{2h}$  symmetry, as shown in Fig. 1. However, some facts do not allow us to consider the data [13,14] as final without any doubts.

In 1978, Hirayama et al. [15] carried out mass spectral investigation of the vapour over  $\text{ScI}_3$  in the temperature range of 766–801 K and an effusion weight loss experiment over the range of 782–872 K. According to the results [15], the  $\text{Sc}_2\text{I}_6$  concentration is 7.02 mol% at 872 K. However, these authors assumed the ratio of ionization cross-sections of  $\text{Sc}_2\text{I}_6$  and  $\text{ScI}_3$  to be 1:1. Later the data [15] were reinterpreted by Work [16] using the ratio of 1.5:1. Although the temperature range in the work [15] is too narrow for an accurate determination of the dependence of  $\text{Sc}_2\text{I}_6$  content on temperature, it may be estimated to be less than 25 mol% at 1050 K [16]. Therefore, the dimer concentration found in study [13] (75 mol% at 1050 K, later specified to be 79(3) mol% in [14]) is inconsistent with mass spectral investigations.

In the present work, a thorough investigation of  $\text{ScI}_3$  structure by synchronous gas-phase electron diffraction and mass spectrometric experiment combined with

the theoretical study of  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules has been carried out.

## 2. Experimental

The synchronous gas-phase electron diffraction and mass spectrometric experiment was carried out on the modified EMR-100/APDM-1 unit [17–19]. A commercial sample of  $\text{ScI}_3$  obtained from Aldrich (99.999% purity) was evaporated at the temperature of 896(10) K from a molybdenum cell with a cylindrical effusion nozzle of  $0.6 \times 1.2$  mm size (diameter  $\times$  length). The ratio of evaporation area to effusion orifice area was above 500. The vapour composition has been monitored by mass spectra during the entire experiment, including the exposure of the diffraction patterns (Kodak electron microscope films were used). Mass spectra of the saturated vapour over  $\text{ScI}_3$  are presented in Table 1. We assumed that all ions except  $\text{Sc}_2\text{I}_5^+$  originated from  $\text{ScI}_3$  monomer only. The ratio of ionization cross-sections of  $\text{Sc}_2\text{I}_6$  and  $\text{ScI}_3$  was assumed to be 2:1. According to the mass spectra a small amount of dimeric molecules was present in the saturated vapour over  $\text{ScI}_3$ —4.0(2) and 3.7(3) mol%, long and short camera distances, respectively (statistical error is given in parentheses). The mass spectral data show the presence of about 2–3 mol% of  $\text{I}_2$  molecules as well. No other volatile admixtures were found in the vapour at the temperature of the diffraction pattern recording.

Electron diffraction patterns were obtained from the short ( $L_1 = 338$  mm) and long ( $L_2 = 598$  mm) camera distances at an accelerating voltage of 70 kV. The wavelength of electrons was calibrated using polycrystalline ZnO. The optical densities were measured by a modified computer controlled MD-100 (Carl Zeiss, Jena) microdensitometer [20]. The initial data processing and the determination of the wavelength of the electrons were performed using the technique described in our study of  $\text{LaCl}_3$  and  $\text{LaBr}_3$  molecules [21].

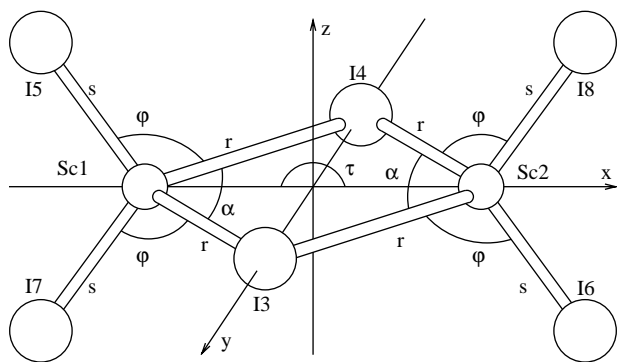


Fig. 1. The view, atomic numbering, and internal coordinates of  $\text{Sc}_2\text{I}_6$  molecule.

Table 1

Mass spectra of the saturated vapour over  $\text{ScI}_3$  (cell temperature 896(10) K, ionizing energy 50 eV) obtained in our study during the exposure of the films (long and short camera distances,  $L = 598$  and 338 mm, respectively) in comparison with the mass spectrum from the work of Hirayama et al. [15]

	Sc	$\text{ScI}^+$	$\text{ScI}_2^+$	$\text{ScI}_3^+$	$\text{Sc}_2\text{I}_5^+$	$T$ (K)
Our study ( $L = 598$ mm)	55 <sup>a</sup>	68	100	52	23	893
Our study ( $L = 338$ mm)	55 <sup>a</sup>	62	100	57	21	899
Hirayama (1978) [15]	224	128	100	44	15	775

<sup>a</sup> The value given in the table was obtained by subtracting the intensities at open and close molecular beam shutter positions.

Table 2

Structural parameters of the  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules obtained from quantum chemical calculations (B3LYP and MP2, present work, and CISD(Q) [9])

	DFT/LanL2DZ	DFT/SDD	DFT/TZV	MP2	CISD(Q) [9]
$r_e(\text{Sc-I})$ (Å)	2.652	2.656	2.656	2.635	2.651
$\alpha_e(\text{I-Sc-I})$ (degrees)	120	120	120	120	120
$r_e(\text{Sc-I}_t)$ (Å)	2.638	2.649	2.653	2.627	–
$r_e(\text{Sc-I}_b)$ (Å)	2.900	2.864	2.869	2.820	–
$\alpha_e(\text{I}_t\text{-Sc-I}_t)$ (degrees)	113.9	115.2	114.7	116.9	–
$\alpha_e(\text{I}_b\text{-Sc-I}_b)$ (degrees)	92.6	93.3	93.4	95.6	–

### 3. Quantum chemical calculations

The geometry optimization and vibrational frequency calculations for the  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules were carried out using the GAUSSIAN 98 [22] and GAMESS [23] programs. We have utilized DFT (B3LYP hybrid functional) and MP2 methods for both monomer and dimer computations. In the first two DFT calculations built-in GAUSSIAN 98 LanL2DZ and SDD basis sets (later depicted as DFT/LanL2DZ and DFT/SDD, respectively) were used. In all other cases (DFT/TZV and MP2, using GAMESS) a valence triple zeta basis set (14s11p6d3f/10s8p3d1f) has been used for describing scandium atoms. It was derived from the Wachters basis set (14s9p5d) [24] contracted to (10s8p3d) with the following modifications [23]: the most diffuse  $s$  function was replaced by  $s$  function with the orbital exponent  $\alpha_s$  of 0.077533 spanning the 3s–4s region; two additional  $p$  functions with  $\alpha_p$  of 0.137 and 0.053 were added to describe the 4p region;  $d$  and  $f$  functions were taken from Refs. [25,26], respectively. Relativistic effects were taken into account according to Ref. [27]. In case of iodine atoms the core shells ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$ ) were described by the Relativistic Effective Core Potential [28] and the (14s10p2d1f/3s3p2d1f) basis set [29] was used for describing the valence shells. The RECP and basis sets were obtained from the database [30].

The structural parameters of  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules obtained by our theoretical investigation and study [9] are compared in Table 2. The calculated vibrational frequencies of scandium triiodide are listed in Table 3. We have also studied the potential of out-of-plane  $\nu_2$  vibration utilizing the MP2 method and the previously mentioned basis sets. The value of the  $\nu_2$  vibrational frequency calculated from this potential using the harmonic oscillator approach ( $65\text{ cm}^{-1}$ ) was found to be slightly higher than the value produced by the built-in GAMESS force field calculation procedure ( $58\text{ cm}^{-1}$ ).

All DFT and MP2 calculations yielded the planar  $D_{3h}$  symmetry structure of  $\text{ScI}_3$  molecule. This conclusion is in agreement with earlier GED investigation [13,14] and ab initio study [9]. According to the results of our theoretical study the  $\text{Sc}_2\text{I}_6$  dimer possesses the  $D_{2h}$  symmetry structure shown in Fig. 1. The results of the earlier GED study [13,14] are in agreement with such a configuration. It is similar to the structures of  $\text{Sc}_2\text{Cl}_6$  [12] and some lanthanide trihalide dimers (GED studies of  $\text{Lu}_2\text{Cl}_6$  [31] and  $\text{Er}_2\text{Br}_6$  [32] and

ab initio investigation of  $\text{La}_2\text{Br}_6$  and  $\text{Dy}_2\text{Br}_6$  [33]). The calculated vibrational frequencies of scandium triiodide dimer are presented in Table 4.

### 4. Structural analysis

A least-squares structure refinement was performed using a modified version of the KCED 35 program [34]. It was assumed that the  $\text{ScI}_3$  molecule has a third-order symmetry axis. The internuclear distances  $r_a(\text{Sc-I})$  and  $r_a(\text{I}\cdots\text{I})$ , r.m.s. amplitudes  $l(\text{Sc-I})$  and  $l(\text{I}\cdots\text{I})$ , the asymmetry constant  $\kappa(\text{Sc-I})$ , and scaling factors were refined as independent parameters;  $\kappa(\text{I}\cdots\text{I})$  was constrained to be zero.

For  $\text{Sc}_2\text{I}_6$  molecule the  $D_{2h}$  symmetry structure with four  $\text{Sc-I}_b$  bridging bonds (Fig. 1) yielded by our theoretical study (see above) has been chosen. It has been described by the following three independent parameters: the non-bonded  $\text{Sc}\cdots\text{Sc}$  and  $\text{I}_b\cdots\text{I}_b$  distances and the  $\text{Sc}\cdots\text{Sc-I}_t$  angle. Due to the low concentration of the dimer and the correlation between the parameters mentioned, they were refined in turn. The difference between the  $\text{Sc-I}$  distance in the monomer and the  $\text{Sc-I}_t$  distance in the dimer was fixed at the value of  $0.008\text{ Å}$  taken from our MP2 results. A coefficient corresponding to the ratio of the molecular species concentrations has also been refined as independent parameter.

The structural refinement of  $\text{Sc}_2\text{I}_6$  data was performed in terms of a geometrically consistent  $r_\alpha$  structure. To transfer the  $r_a$  parameters to  $r_\alpha$  we used the set of corrections calculated from the force field obtained in the MP2 computation by utilizing the SHRINK program (second approximation, taking into consideration non-linear terms in the transformation between the Cartesian and internal

Table 3

Vibrational frequencies (in  $\text{cm}^{-1}$ ) of the  $\text{ScI}_3$  molecule obtained from quantum chemical calculations (B3LYP and MP2, present work, and CISD(Q) [9]) and spectroscopic study [10]

Method	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$
DFT/LanL2DZ	141	23	317	41
DFT/SDD	148	51	323	42
DFT/TZV	149	53	324	44
MP2	157	58	345	44
CISD(Q) [9]	159	67	346	47
IR spectrum [10]			266	

Table 4

Vibrational frequencies (in  $\text{cm}^{-1}$ ) of the  $\text{Sc}_2\text{I}_6$  molecule obtained from quantum chemical calculations (B3LYP and MP2)

Mode	Symmetry	Frequency ( $\text{cm}^{-1}$ )				IR intensity (km/mole) (MP2 study)
		DFT/ /LanL2DZ	DFT/SDD	DFT/TZV	MP2	
1	$A_g$	288	290	289	310	–
2	$A_g$	120	131	129	140	–
3	$A_g$	71	73	73	76	–
4	$A_g$	32	32	32	32	–
5	$B_{1g}$	150	169	166	190	–
6	$B_{1g}$	45	50	48	50	–
7	$B_{2g}$	305	311	311	336	–
8	$B_{2g}$	32	36	38	38	–
9	$B_{3g}$	31	34	34	36	–
10	$A_u$	19	19	20	21	–
11	$B_{1u}$	310	316	315	340	195
12	$B_{1u}$	47	51	51	52	0.04
13	$B_{1u}$	7	5	12	2	0.1
14	$B_{2u}$	202	227	228	253	45
15	$B_{2u}$	31	34	35	37	2
16	$B_{3u}$	259	265	263	283	225
17	$B_{3u}$	114	125	122	132	5
18	$B_{3u}$	45	44	45	45	0.5

coordinates) [35]. The starting values of r.m.s. amplitudes were also taken from this calculation. The amplitudes were refined in groups corresponding to the different peaks on the radial distribution curve. We also tried to refine the data taking into account the presence of  $\text{I}_2$  molecules in the vapour but it did not have any influence on the disagreement factor and/or any structural parameters.

The thermal average  $r_a$  parameters obtained by the refinement of the experimental data both with and without taking into account the presence of dimeric species in the vapour are given in Table 5. The experimental and calculated molecular intensity  $sM(s)$  curves and the difference curves (a) are shown in Fig. 2. The two curves at the bottom (b) represent the difference curves calculated

with the dimer deducted. The experimental and calculated radial distribution curves are presented in Fig. 3. Table 6 compiles the thermal average  $r_g$  structural parameters of  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules in comparison with the quantum chemical data and the results of the study [13,14].

## 5. Results and discussion

### 5.1. Spectroscopic data and vibrational frequencies

Only one spectroscopic study of the  $\text{ScI}_3$  molecule in the gas-phase exists [10]. One broad ( $\Delta\nu_{1/2} = 30 \text{ cm}^{-1}$ ) band at  $266 \text{ cm}^{-1}$  was present in the absorption spectrum recorded

Table 5

Results of structure refinement of the gas-phase electron diffraction experimental data on the  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules<sup>a</sup>

	$\text{ScI}_3^b$			$\text{ScI}_3 + \text{Sc}_2\text{I}_6^c$		
$s$ range ( $\text{\AA}^{-1}$ )	1.4–15.1	3.6–25.9	1.4–25.9	1.4–15.1	3.6–25.9	1.4–25.9
$r_a(\text{Sc–I})$ ( $\text{\AA}$ )	2.6521(5)	2.6507(5)	2.6516(5)	2.6490(5)	2.6465(3)	2.6473(3)
$r_a(\text{I} \cdots \text{I})$ ( $\text{\AA}$ )	4.5008(22)	4.5031(25)	4.5020(17)	4.5115(23)	4.5157(25)	4.5134(18)
$L(\text{Sc–I})$ ( $\text{\AA}$ )	0.0875(8)	0.0856(5)	0.0864(4)	0.0853(8)	0.0834(4)	0.0836(4)
$l(\text{I} \cdots \text{I})$ ( $\text{\AA}$ )	0.2976(19)	0.3060(16)	0.3013(12)	0.2933(19)	0.3051(15)	0.2986(13)
$k(\text{Sc–I})$ ( $\text{\AA}^3$ )	$1.3 \times 10^{-5}$ <sup>d</sup>	$1.1(3) \times 10^{-5}$	$1.3(3) \times 10^{-5}$	0 <sup>e</sup>	0 <sup>e</sup>	0 <sup>e</sup>
$R_f$ (%)	3.6	4.4	4.2	3.5	4.1	4.1
$\chi_{\text{dim}}$ (mol%)	0	0	0	3.0(3)	3.4(3)	3.4(2)
$r_a(\text{Sc–I}_b)$ ( $\text{\AA}$ )	–	–	–	2.798(22)	2.842(16)	2.819(12)
$\angle_a(\text{Sc} \cdots \text{Sc–I}_b)$ (degrees)	–	–	–	123.1(22)	122.6(34)	123.0(25)
$l(\text{Sc–I}_b)$ ( $\text{\AA}$ )	–	–	–	0.1223(8)	0.1204(4)	0.1206(4)
$l(\text{I}_b \cdots \text{I}_b)$ ( $\text{\AA}$ )	–	–	–	0.2933(19)	0.3051(15)	0.2986(13)
$l(\text{I}_b \cdots \text{I}_b)$ ( $\text{\AA}$ )	–	–	–	0.1833(19)	0.1951(15)	0.1886(13)
$l(\text{Sc} \cdots \text{Sc})$ ( $\text{\AA}$ )	–	–	–	0.1933(19)	0.2051(15)	0.1986(13)

<sup>a</sup>  $\sigma_{\text{LS}}$  is given in parentheses.

<sup>b</sup> Refinement with assumption that only monomer was present in the vapour.

<sup>c</sup> Refinement with assumption that vapour contained both monomer and dimer.

<sup>d</sup> Fixed, cannot be determined.

<sup>e</sup> Constrained to zero because all refinements yielded  $k(\text{Sc–I})$  value equal to zero within  $\sigma_{\text{LS}}$ .



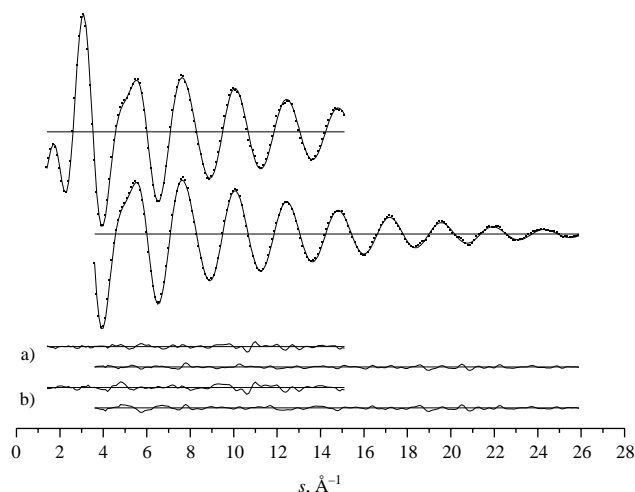


Fig. 2. Experimental (dots) and theoretical (lines) molecular intensity curves  $sM(s)$ , difference curves (a), and difference curves calculated with the dimer deducted (b).

at a temperature of about 1100 K. The author [10] assigned it to the  $\nu_3$  vibrational frequency of the  $\text{ScI}_3$  molecule. Ezhov and Sevastyanov [36] also studied the IR spectrum of  $\text{ScI}_3$  solution in benzene. According to [36]  $\text{Sc}_2\text{I}_6$  was the major molecular species in the solution. A weak band at  $265\text{ cm}^{-1}$  was assigned by the authors to the  $\nu_3$  vibrational frequency of  $\text{ScI}_3$ .

The two theoretical studies—the present theoretical investigation and the ab initio study [9] give significantly different value of the  $\nu_3$  vibrational frequency: 324 (DFT/TZV), 345 (MP2), and 346 (CISD(Q)  $\text{cm}^{-1}$ ) [9]. Moreover, the calculation of the r.m.s. amplitudes using the value of  $\nu_3 = 266\text{ cm}^{-1}$  produces unreasonably large value of  $l(\text{Sc}-\text{I}) = 0.105\text{ Å}$ , which is inconsistent with our GED data. One possible explanation of such disagreement may be the following: the bands at about  $265\text{ cm}^{-1}$  observed in [10,36] should be assigned to the Sc–I asymmetric stretching vibration in the dimer species rather than to the  $\nu_3$  vibrational frequency of the  $\text{ScI}_3$  molecule. The IR spectrum

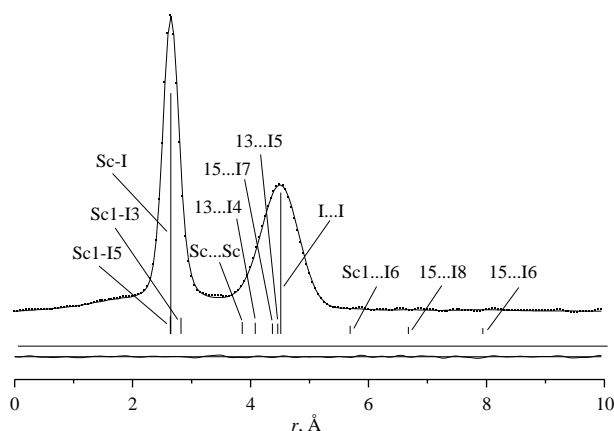


Fig. 3. Experimental (dots) and theoretical (line) radial distribution curves  $f(r)$  and difference curve (below).

of the  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  mixture (1:1 ratio) calculated in our MP2 theoretical study is presented in Fig. 4. The frequency of  $283\text{ (MP2) cm}^{-1}$  (mode no. 16 of  $\text{Sc}_2\text{I}_6$  molecule, see Table 4) is one of the most intense in the IR spectrum of  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$ , along with the  $\nu_3$  frequency of  $\text{ScI}_3$  ( $345\text{ cm}^{-1}$ ) and mode no. 11 of  $\text{Sc}_2\text{I}_6$  ( $340\text{ cm}^{-1}$ ). Unfortunately, the region of the  $\text{ScI}_3/\text{Sc}_2\text{I}_6$  IR spectrum ( $320\text{--}350\text{ cm}^{-1}$ ) where one may expect to find the  $\nu_3$  frequency of the  $\text{ScI}_3$  molecule is not presented in the work [10] at all.

At first it seems that the data on the vapour composition over  $\text{ScI}_3$  [15,16] do not support the hypothesis about the assignment of the frequency of  $265\text{ cm}^{-1}$  found in [10] to dimeric species, giving the dimer concentration of less than 30 mol% at 1100 K (the experimental temperature in study [10]). However, the experiment in work [10] was carried out with the use of a non-isothermal graphite cell and the condensation of the vapour could result in the appearance of the oligomeric species. In such case it seems to be possible that the band corresponding to the dimer vibration mentioned above could be one of the most intense and Selivanov [10] incorrectly assigned it to the  $\nu_3$  frequency of the monomer.

The set of vibrational frequencies yielded by our ab initio MP2 study (see Table 3) has been used for calculation of theoretical r.m.s. amplitudes and shrinkage of the I...I distance (which will be discussed in detail later). As shown in Table 6, all of our experimental values are close to the calculated ones, in contrast to the  $l(\text{I}-\text{I})$ ,  $l(\text{Sc}-\text{I}_i)$ ,  $l(\text{Sc}\cdots\text{Sc})$ ,  $l(\text{I}_i\cdots\text{I}_i)$  values presented in the study [13,14]. It should also be noted that the frequencies obtained in the ab initio study [9], with the use of a different method and basis sets, are almost identical to our values. Thus, this set of vibrational frequencies of  $\text{ScI}_3$  molecule may probably be considered as the most reliable.

## 5.2. Vapour composition

In our study, the concentration of dimer species has been independently determined by mass-spectrometry and GED data refinement. Both approaches yielded similar results (3.7–4.0 and 3.5(7) mol% from mass spectra and GED, respectively). Moreover, it is also in agreement with the study [15] carried out in 1978 by Hirayama et al.

According to the results [15], the  $\text{Sc}_2\text{I}_6$  concentration is 7.02 mol% at 872 K. However, it was calculated assuming the ratio of ionization cross-sections of  $\text{Sc}_2\text{I}_6$  and  $\text{ScI}_3$  to be 1:1. Later Work [16] pointed out that such assumption is incorrect and reinterpreted the data [15] using the ratio of 1.5:1. At the same time, recent synchronous GED/MS studies of rare earth metal trihalides [12,31,32] have shown the ratio of ionization cross-sections of  $\text{M}_2\text{X}_6$  and  $\text{MX}_3$  as 2:1 providing good agreement between GED and MS data on dimer content.

If the dimer concentration in our study and in the work [15] is calculated assuming the same ratio of ionization cross-sections, the results are in good agreement (e.g. use of

Table 6

Structural parameters of the  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  molecules obtained from gas-phase electron diffraction and ab initio studies

GED, our study		MP2, our study		GED, [13,14]		
<i>Distances and r.m.s. amplitudes</i>						
	$r_g$ (Å)	$l$ (Å)	$r_e$ (Å)	$l$ (Å)	$r_g$ (Å)	$l$ (Å)
Sc–I	2.650(5)	0.084(2)	2.635	0.086	2.62(2)	0.08 <sup>a,b</sup>
I···I	4.533(10)	0.299(4)	4.563	0.292	4.47(5)	0.17(5) <sup>b</sup>
Sc–I <sub>t</sub>	2.643(5)	0.084(2)	2.627	0.087	2.62(1)	0.11 <sup>a,c</sup>
Sc–I <sub>b</sub>	2.82(3)	0.121(2)	2.820	0.122	2.75(1)	0.13 <sup>a,c</sup>
Sc···Sc	3.87(5)	0.199(4)	3.788	0.204	3.20(1)	0.14(3) <sup>c</sup>
I <sub>b</sub> ···I <sub>b</sub>	4.09(5)	0.189(4)	4.178	0.191	4.47(4)	0.17(4) <sup>c</sup>
I <sub>t</sub> ···I <sub>t</sub>	4.39 <sup>d</sup>	0.299(4)	4.478	0.298	4.71(3)	0.25(5) <sup>c</sup>
I <sub>b</sub> ···I <sub>t</sub>	4.49 <sup>d</sup>	0.369(4)	4.479	0.367	4.25(1)	0.20(2) <sup>c</sup>
<i>Valence angles</i>						
	$\angle_g$ (degrees)	$\angle_\alpha$ (degrees)	$\angle_e$ (degrees)		$\angle_g$ (degrees)	$\angle_\alpha$ (degrees)
I–Sc–I	117.6(4)		120		117.1	
Sc–I <sub>b</sub> –Sc		86.7(10)	84.4		71(2)	
I <sub>t</sub> –Sc–I <sub>t</sub>		114(8)	116.9		128.2(5)	

<sup>a</sup> Fixed value.<sup>b</sup> Cited in Ref. [13].<sup>c</sup> Cited in Ref. [14].<sup>d</sup> Dependent parameter.

the 2:1 ratio gives  $3.9 \pm 0.6$  mol% from our data and 3.5 mol% from the data [15]). The mass spectra obtained in our study and investigation [15] are similar (see Table 1) except the large difference in  $\text{Sc}^+$  and  $\text{ScI}^+$  intensities, which is probably the result of mass discrimination of the time-of-flight mass spectrometer used by Hirayama et al. [15]. Taking into account such discrimination should make the mass spectrum [15] more similar to our data.

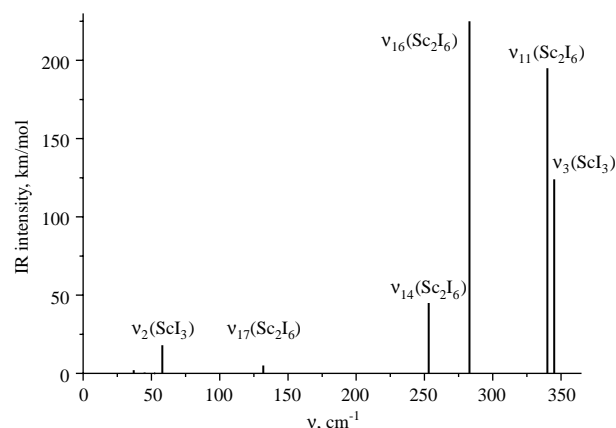
On the other hand, the dimer concentration found in study [13] (75 mol% at 1050 K, later specified to be 79(3) mol% in [14]) is inconsistent with mass spectral investigations. The authors [13] determined the vapour composition by the refinement of the GED data (within narrow  $s$  range of  $2.0$ – $16.0 \text{ Å}^{-1}$ ) with fixed r.m.s. amplitudes values ( $0.08$ – $0.09 \text{ Å}$  for all Sc–I bonded distances and  $0.2 \text{ Å}$  for all other distances). The latter value is clearly underestimated by at least  $0.1 \text{ Å}$  in case of all non-bonded distances except  $\text{Sc} \cdots \text{Sc}$  and  $\text{I}_b \cdots \text{I}_b$  in the dimer (see Table 6). This is probably the result of incorrect estimations of vibrational frequencies. Ezhov et al. [13] calculated r.m.s. amplitudes using the unspecified frequencies of the  $\text{ScI}_3$  molecule estimated using the spectroscopic data on  $\text{ScF}_3$  and the value of  $\nu_3 = 266 \text{ cm}^{-1}$  of  $\text{ScI}_3$  from [10]. The final refinement of structural parameters of the monomer and dimer species in [13] was carried out using the fixed vapour composition obtained in the previous step.

Later, in the work [14] (concerning mostly  $\text{Sc}_2\text{I}_6$ ) Ezhov et al. provided the following estimated frequencies of  $\text{ScI}_3$ :  $\nu_1 = 125$ ,  $\nu_2 = 105$ ,  $\nu_3 = 265$ , and  $\nu_4 = 45 \text{ cm}^{-1}$ . These values strongly disagree (except  $\nu_4$ ) with the results of our theoretical study as well as with data [9] (see Table 3). The incorrect assignment of the band at  $\sim 265 \text{ cm}^{-1}$  to the  $\nu_3$  vibrational frequency of the  $\text{ScI}_3$  molecule in [10] is discussed above. The form of the molecular intensity  $sM(s)$  curve given in [14] indicates the presence of a large amount

of molecular species different from  $\text{ScI}_3$  (dimer according to the authors [14]), and we do not have a satisfactory explanation of such huge amount of dimer species.

### 5.3. Molecular structure

Structural refinement of the gas-phase electron diffraction data for  $\text{ScI}_3$  yielded the thermal average structure of  $C_{3v}$  symmetry with  $\angle_g(\text{I}–\text{Sc}–\text{I})$  bond angle of  $117.6(4)^\circ$ . The fact that this value is very close to  $120^\circ$  allows one to suggest that the  $\text{ScI}_3$  molecule may possess a planar equilibrium structure. In this case, the deviation of the bond angle value from  $120^\circ$  should be solely caused by shrinkage effect of the  $\text{I} \cdots \text{I}$  distance. In order to test such a hypothesis, experimental and calculated shrinkage values should be compared. Due to the lack of experimentally determined vibrational frequencies of  $\text{ScI}_3$  we had to use the force field obtained in the ab initio part of our study

Fig. 4. Calculated IR spectrum of the 1:1 mixture of  $\text{ScI}_3$  and  $\text{Sc}_2\text{I}_6$  species.

(see Table 3 for the sets of calculated frequencies) for the calculation of the theoretical shrinkage effect.

The shrinkage value calculated in the harmonic approximation using the frequencies from our MP2 study  $\delta(\text{I}\cdots\text{I})=0.066\text{ \AA}$  is equal to the experimental one  $\delta_{\text{exp}}(\text{I}\cdots\text{I})=0.060(8)\text{ \AA}$  within the uncertainty limit. The equilibrium value of the bond angle calculated in the harmonic approximation  $\angle_{\alpha}(\text{I}-\text{Sc}-\text{I})=120.4(4)^{\circ}$  is equal to  $120^{\circ}$  (corresponding to planar  $D_{3h}$  symmetry structure). The calculation using frequencies from our DFT studies gave larger values that are physically unreasonable. It clearly shows that the frequencies calculated by the DFT approach are underestimated and should not be used without scaling.

The fact that the theoretical shrinkage value is equal to the one experimentally determined means that the deviation of the thermal average bond angle value from  $120^{\circ}$  could be totally ascribed to the shrinkage effect of the  $\text{I}\cdots\text{I}$  distance. Thus, the results of our investigations, both experimental and theoretical, allow us to conclude that the equilibrium geometry of scandium triiodide molecule is planar ( $D_{3h}$  symmetry). This is in agreement with the results of earlier GED [13,14] and theoretical [9] studies.

In this study we have obtained the thermal average value of the Sc–I bond length  $r_{\text{g}}(\text{Sc}-\text{I})=2.650(5)\text{ \AA}$  at  $T=896(10)\text{ K}$ . It is significantly (by  $0.03\text{ \AA}$ ) larger than the value determined in study [13] at higher temperature ( $T=1050\text{ K}$ ). However, the value of  $r_{\text{g}}(\text{Sc}-\text{I})$  found in [13] ( $2.62(2)\text{ \AA}$ ) has a large uncertainty that almost overlaps the difference. Again, the main reason for such disagreement may be a wrong assumption about the vapour composition in the study [13]. There is a strong correlation between the concentration of the dimeric species and the value of  $r_{\text{a}}(\text{Sc}-\text{I})$  yielded by the refinement because the Sc–I and Sc–I<sub>b</sub> distances are represented by a single peak on the radial distribution curve and therefore cannot be determined independently. The vapour composition and the values of the  $l(\text{Sc}-\text{I})$  and  $l(\text{Sc}-\text{I}_b)$  r.m.s. amplitudes are also strongly correlated. For example, when the vapour composition,  $r(\text{Sc}-\text{I})$  and  $l(\text{Sc}-\text{I})$  are refined simultaneously, the correlation coefficients between vapour composition and  $r(\text{Sc}-\text{I})$  and  $l(\text{Sc}-\text{I})$  are larger than 0.7 and 0.6, respectively. We have found that the data refinement with the assumption of a simple vapour composition (only monomer is present) gives  $r_{\text{g}}(\text{Sc}-\text{I})$  elongated by  $0.004\text{ \AA}$ . Therefore, a significant overestimation of dimer concentration in [13,14] could give a significantly shortened value of  $r_{\text{g}}(\text{Sc}-\text{I})$ .

The concentration of dimeric species in the saturated vapour over  $\text{ScI}_3$  at the temperature of our experiment is rather small. Nevertheless, it was possible to determine the basic structural parameters of  $\text{Sc}_2\text{I}_6$  molecule, although with large uncertainties. Our results of GED data refinement are well consistent with our MP2 study of the dimer. The difference between Sc–I<sub>t</sub> and Sc–I<sub>b</sub> bond length  $\Delta r_{\text{exp}}=0.18(4)\text{ \AA}$  is in good agreement with the value from MP2 calculation ( $\Delta r=0.193\text{ \AA}$ ). According to the data [14]

the difference between  $r_{\text{a}}(\text{Sc}-\text{I}_b)$  and  $r_{\text{a}}(\text{Sc}-\text{I}_t)$  distances is  $0.13\text{ \AA}$ . At the same time it is well known that such difference between bridging and terminal M–X distances in  $\text{M}_2\text{X}_6$  dimers of metal trihalides is typically ca.  $0.2\text{ \AA}$  [12,31,37,38]. Hence, the difference between  $r_{\text{a}}(\text{Sc}-\text{I}_b)$  and  $r_{\text{a}}(\text{Sc}-\text{I}_t)$  distances of  $0.13\text{ \AA}$  reported in [14] is incorrect and probably is a result of a significant overestimation of dimer concentration. This conclusion is also supported by the fact that all parameters of the Sc–I–Sc–I cycle presented in [14] are very different from our ab initio results, especially the unreasonable value of  $r_{\text{g}}(\text{Sc}\cdots\text{Sc})=3.20(1)\text{ \AA}$  which is shorter than ab initio  $r_{\text{e}}$  value of  $3.788$  by almost  $0.6\text{ \AA}$ .

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