Zirconium chloride molecular species: combining electron impact mass spectrometry and first principles calculations

Rosendo Borjas Nevarez¹ · Eunja Kim² · Bradley C. Childs³ · Henrik Braband³ · Laurent Bigler³ · Urs Stalder³ · Roger Alberto³ · Philippe F. Weck⁴ · Frederic Poineau¹

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Abstract

Zirconium tetrachloride was synthesized from the reaction between zirconium metal and chlorine gas at 300 °C and was analyzed by electron impact mass spectrometry (EI-MS). Substantial fragmentation products of ZrCl_4 were observed in the mass spectra, with ZrCl_3 being the most abundant species, followed by ZrCl_2 , ZrCl , and Zr . The predicted geometry and kinetic stability of the fragments previously mentioned were investigated by density functional theory (DFT) calculations. Energetics of the dissociation processes support the most stable fragment to be ZrCl_3 while the least abundant are ZrCl and ZrCl_2 .

Keywords Zirconium · Chloride · Mass spectrometry · Gas phase · DFT

1 Introduction

Zirconium chloride is of crucial importance in numerous research fields and industrial applications such as unconventional catalysis [1], refining of Zr-containing ores by Kroll reduction [2], chemical vapor deposition [3], and nuclear engineering [4–6]. Chlorination has been proposed for large-scale separation and selective recovery of Zr as ZrCl_4 from U–Zr alloys or used nuclear fuel cladding [4, 5]. Due to the presence of impurities (e.g., Sn, Cr, Fe, etc.) in the recovered ZrCl_4 , further efforts are necessary to improve the purification process. This requires fundamental understanding of the materials during each stage of the process. Starting materials consist of Zr cladding such as Zircaloy-4, Zircaloy-2 and Zr–Nb alloys (Zirlo™ and Zr-2.5Nb) while the final product should be Zr metal. In the chlorination process, the intermediate material is ZrCl_4 . Our previous efforts have been devoted on fundamental studies of the starting materials described above

[7], followed by ZrCl_4 [8, 9]. Therefore, an accurate knowledge of zirconium chlorides is crucial for efficient separation and selective recovery of Zr from cladding materials. While much attention has been given to the theoretical and experimental investigations of crystalline ZrCl_4 [9], accurate structural and thermomechanical information of ZrCl_x ($x = 1, 2, 3, 4$) molecular species remains scarce. Due to their chemical similarities and the importance of the refinement process in the nuclear industry, studies on gaseous ZrCl_4 are typically performed in conjunction with HfCl_4 . The first electronographic approximations calculated the theoretical intensity curves based on the intermolecular distances in ZrCl_4 (i.e. $\text{Zr–Cl} = 2.32 \text{ \AA}$ and $\text{Cl}\cdots\text{Cl} = 3.79 \text{ \AA}$) and in HfCl_4 (i.e. $\text{Hf–Cl} = 2.33 \text{ \AA}$ and $\text{Cl}\cdots\text{Cl} = 3.80 \text{ \AA}$) [10]. Recently, Barnes et al. reported that the vapor pressure of ZrCl_4 , FeCl_3 , CrCl_4 , NbCl_5 , and NbOCl_3 are very similar at temperatures near 330 °C [11]. The vapor pressure of ZrCl_4 has also been measured under vacuum and under argon atmospheres [12]. In addition, DFT models have been used

✉ Rosendo Borjas Nevarez, borjasr@unlv.nevada.edu | ¹Department of Chemistry and Biochemistry, University of Nevada, Las Vegas, 4505 S. Maryland Pkwy, Las Vegas, NV 89154, USA. ²Department of Physics and Astronomy, University of Nevada, Las Vegas, 4505 S. Maryland Pkwy, Las Vegas, NV 89154, USA. ³Department of Chemistry, University of Zurich, Rämistrasse 71, 8006 Zurich, Switzerland. ⁴Sandia National Laboratories, Albuquerque, NM 87185, USA.

to predict the volatility and adsorption enthalpies of ZrCl_4 , ZrOCl_2 , and ZrCl_6^{2-} salts in comparison to the other Group IV metal chlorides. These models are for the most part in disagreement with experimental data [13], demonstrating the complexity of these gas phase interactions. As for gaseous ZrCl_2 , the structure, vibrational frequencies, and heat of formation have been predicted, and they are in close agreement with experimental data [14].

In this study, we have carried out combined experimental and computational studies to investigate the structures, electronic properties, and relative stability of the ZrCl_x ($x = 1, 2, 3, 4$) molecules in the gas phase.

2 Experimental

2.1 Preparation of sample

Zirconium metal sponge (> 99% purity), and a lecture bottle of chlorine gas (> 99.5% purity) were obtained from Sigma Aldrich and used as received. The clamshell furnace was a Lindberg Blue M Mini-Mite.

ZrCl_4 was synthesized from the reaction of zirconium metal and chlorine gas at 300 °C in a glass sealed tube according to the method reported in the literature [9]. After the reaction, the end of the tube containing ZrCl_4 was placed in liquid nitrogen and the tube was sealed to separate the zirconium oxide impurity. The capillary was then checked for external contamination and sent to the University of Zurich.

2.2 Analysis of sample

At the University of Zurich, the sealed tube was stored in an inert atmosphere (N_2) glove box. The tube was opened in the glovebox and ZrCl_4 samples were placed in sample holders. The samples were then transferred to a Schlenk flask and sealed. The sample was introduced into a glove bag system, which was installed in front of the mass spectrometer and included the sample inlet. The system was evacuated and then purged with argon three times before opening the Schlenk flask. The ZrCl_4 sample was mounted on the probe, which was then inserted into the mass spectrometer to be measured. Mass spectrometry measurements were performed on a Thermo DFS (ThermoFisher Scientific, Bremen, Germany) double-focusing magnetic sector mass spectrometer (geometry BE). Mass spectra were measured in electron impact mode at 70 eV, with a solid probe inlet, source temperature of 50 °C, acceleration voltage of 5 kV, and a resolution of 7000. The instrument was scanned from $m/z = 30$ to 800 at a scan rate of 2 s per decade in the magnetic scan mode, and temperature ramp rate was 60 °C per minute until 400 °C was reached.

Perfluorokerosene (PFK, Fluorochem, Derbyshire, UK) was used for mass calibration.

2.3 Computational method

First-principles all-electron calculations of the total energies and optimized geometries were performed using the density functional theory (DFT) as implemented in the DMol³ software [15]. The exchange correlation energy was calculated using the generalized gradient approximation (GGA) with the parametrization of Perdew and Wang [16] (PW91). Double numerical basis sets including polarization functions on all atoms (DNP) were used in the calculations. The DNP basis set is comparable to 6-31G** Gaussian basis sets. In the generation of the numerical basis sets, a global orbital cutoff of 3.7 Å was used. The energy tolerance in the self-consistent field calculations was set to 10^{-6} Hartree. Optimized geometries were obtained without symmetry constraints using an energy convergence tolerance of 10^{-5} Hartree and a gradient convergence of 2×10^{-3} Hartree/Å.

3 Results and discussion

3.1 Electron impact mass spectrometry

Zirconium chloride species yield EI-MS peaks that are recognized not only by their mass to charge ratio, but also by their unique splitting pattern due to the isotopic abundances of Zr and Cl (Table 1). The spectrum after a retention time of 6.86 min (400 °C) is presented in Fig. 1. The relative abundances of the observed species were determined from the sum of all the peak counts in the isotopic mass range. In addition to the parent ZrCl_4 molecule, the following fragments are present in a quantifiable manner:

Table 1 Splitting of a ZrCl_4 peak from $m/z = 229.8$ to $m/z = 239.8$ due to isotopic abundance

m/z	Isotopic distribution
229.8	$^{90}\text{Zr}^{35}\text{Cl}_4$
230.8	$^{91}\text{Zr}^{35}\text{Cl}_4$
231.8	$^{90}\text{Zr}^{35}\text{Cl}_3^{37}\text{Cl}$ $^{92}\text{Zr}^{35}\text{Cl}_4$
232.8	$^{91}\text{Zr}^{35}\text{Cl}_3^{37}\text{Cl}$
233.8	$^{92}\text{Zr}^{35}\text{Cl}_3^{37}\text{Cl}$ $^{94}\text{Zr}^{35}\text{Cl}_4$ $^{90}\text{Zr}^{35}\text{Cl}_2^{37}\text{Cl}_2$
234.8	$^{91}\text{Zr}^{35}\text{Cl}_2^{37}\text{Cl}_2$
235.8	$^{94}\text{Zr}^{35}\text{Cl}_3^{37}\text{Cl}$ $^{96}\text{Zr}^{35}\text{Cl}_4$ $^{92}\text{Zr}^{35}\text{Cl}_2^{37}\text{Cl}_2$ $^{90}\text{Zr}^{35}\text{Cl}^{37}\text{Cl}_3$
236.8	$^{91}\text{Zr}^{35}\text{Cl}^{37}\text{Cl}_3$
237.8	$^{96}\text{Zr}^{35}\text{Cl}_3^{37}\text{Cl}$ $^{94}\text{Zr}^{35}\text{Cl}_2^{37}\text{Cl}_2$ $^{92}\text{Zr}^{35}\text{Cl}^{37}\text{Cl}_3$ $^{90}\text{Zr}^{37}\text{Cl}_4$
238.8	$^{91}\text{Zr}^{37}\text{Cl}_4$
239.8	$^{96}\text{Zr}^{35}\text{Cl}_2^{37}\text{Cl}_2$ $^{94}\text{Zr}^{35}\text{Cl}^{37}\text{Cl}_3$ $^{92}\text{Zr}^{37}\text{Cl}_4$

3277ale #143-148 RT: 6.77-7.01 AV: 6 NL: 1.15E7
T: + c EI Full ms [49.50-1000.50]

Fig. 1 Electron impact mass spectra (70 eV) of ZrCl_4 between $m/z=50$ and $m/z=440$

Table 2 Relative abundance of zirconium chloride fragments in the EI-MS spectra of ZrCl_4

Peak range (m/z)	Molecule	Intensity	Abundance (normalized) (%)
89.9	Zr^+	1,228,923.2	1.92
97.2–99.3	ZrCl_3^{2+}	1,836,960.4	2.87
124.9–128.9	ZrCl^+	5,168,760.7	8.09
159.8–165.8	ZrCl_2^+	7,295,977.8	11.4
194.8–202.8	ZrCl_3^+	25,427,641.7	39.8
229.8–239.8	ZrCl_4^+	22,938,047.9	35.9
Total		63,896,311.7	100

ZrCl_3^+ , ZrCl_3^{2+} , ZrCl_2^+ , ZrCl^+ , and Zr^+ (Table 2), with ZrCl_3 clearly as the most abundant species. It is noted that ZrCl_3 is also found in the separation of HfCl_4 from ZrCl_4 using molten salts [17]. The presence of ZrCl_4^{2+} , ZrCl_2^{2+} , and ZrCl^{2+} is also noticed in the EI-MS spectra of ZrCl_4 while the dimeric species Zr_2Cl_7^+ ($m/z \sim 425$) [18] could not be identified in our experimental conditions.

A previous EI-MS study on ZrCl_4 by Schäfer detected the fragments: ZrCl_3^{2+} , Zr^+ , ZrCl^+ , ZrCl_2^+ , ZrCl_3^+ , and Zr_2Cl_7^+ . Also, the mass spectra revealed dimerization of ZrCl_4 to $(\text{ZrCl}_4)_2^+$ with a $(\text{ZrCl}_4)_2^+/\text{ZrCl}_4^+$ ratio of 0.000401 at 459 K [18]. Our data supports the favorable formation of the lower mass fragments. Interestingly, fragments with m/z ratios higher than the mass of ZrCl_4 are also observed at $m/z \sim 385$ but those ratios do not agree with any of the previous findings or with the sum of any combination of Zr and Cl atomic masses.

3.2 Computational studies

Systematic studies to investigate the stable geometries of the neutral and ionic ZrCl_x species has been carried out using density-functional theory (DFT), as implemented in Dmol³ [17] within the level of DFT-PW91 [16], as summarized in Fig. 2. The theoretically optimized geometries indicate that ZrCl is a linear molecule with $\text{Zr}-\text{Cl}=2.37$ Å. It is worth noting that the predicted ZrCl_2 is in C_{2v} with an average $\text{Zr}-\text{Cl}=2.38$ Å. The optimized structure of ZrCl_3 is planar in C_{3v} with $\text{Zr}-\text{Cl}=2.35$ Å. The gaseous

Fig. 2 Ball and stick models of theoretically optimized ZrCl_x molecules: **a** ZrCl , **b** ZrCl_2 , **c** ZrCl_3 , and **d** ZrCl_4 . Cyan and green spheres represent Zr and Cl atoms, respectively

ZrCl_4 is stabilized in the tetrahedral (T_d) structure with $\text{Zr}-\text{Cl}=2.34 \text{ \AA}$, which is nearly identical to the $2.32 \text{ \AA}$ and $2.33 \text{ \AA}$ previously reported for ZrCl_4 and HfCl_4 [10]. The $\text{Zr}-\text{Cl}$ bond distances of the respective ionic forms are slightly shorter, $2.29 \text{ \AA}$ (ZrCl^+), $2.30 \text{ \AA}$ (ZrCl_2^+), $2.32 \text{ \AA}$ (ZrCl_3^+), and $2.36 \text{ \AA}$ (ZrCl_4^+), decreasing by no more than $0.08 \text{ \AA}$ with respect to the neutral species. The most

noticeable change in geometry occurs in the ZrCl_2 bond angle, 135.9° in the neutral form and 110° in the ionic form.

The kinetic stability of these ZrCl_x species was evaluated in terms of the energy gap between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). The calculated HOMO and LUMO for ZrCl_x are presented in Fig. 3. The top and bottom panels depict the HOMO and LUMO of the molecules, respectively, indicating that the major contribution to HOMO of ZrCl_2 , ZrCl_3 , and ZrCl_4 is from Cl-p orbitals while its counterpart to LUMO is mainly from Zr-d orbitals.

The calculated HOMO–LUMO gaps are 0.46 eV (ZrCl), 3.84 eV (ZrCl_2), 3.53 eV (ZrCl_3), and 4.35 eV (ZrCl_4), suggesting ZrCl_4 to be the most stable species and ZrCl the least stable species. The HOMO–LUMO gaps of the corresponding ionic species are 3.98 eV (ZrCl^+), 3.44 eV (ZrCl_2^+), 3.21 eV (ZrCl_3^+), and 4.39 eV (ZrCl_4^+), respectively. A substantial amount of charge transfer from Zr to Cl occurs in these molecular species, $0.47e$ (ZrCl), $0.47e$ (ZrCl_2), $0.43e$ (ZrCl_3), and $0.36e$ (ZrCl_4). Charge transfer of the corresponding ionic species is estimated to be $0.26e$ (ZrCl^+), $0.23e$ (ZrCl_2^+), $0.21e$ (ZrCl_3^+), and $0.13e$ (ZrCl_4^+). The difference in charge transfer shows that $\text{Zr}-\text{Cl}$ bonds are stronger in the neutral species. The calculated structural data and energetics of neutral and ionic ZrCl_x molecules are summarized in Table 3.

Fig. 3 The calculated highest occupied molecular orbitals (HOMO, top) and lowest unoccupied molecular orbitals (LUMO, bottom) of **a** ZrCl , **b** ZrCl_2 , **c** ZrCl_3 , and **d** ZrCl_4

Table 3 Calculated $\text{Zr}-\text{Cl}$ distance ($\text{\AA}$), bond angle ($^\circ$), charge transfer (e) and HOMO–LUMO gap (eV) for ZrCl , ZrCl_2 , ZrCl_3 , ZrCl_4 molecular and the corresponding ionic species. The value in the parenthesis is from Ref [13]

	Neutral species				Ionic species			
	ZrCl	ZrCl_2	ZrCl_3	ZrCl_4	ZrCl^+	ZrCl_2^+	ZrCl_3^+	ZrCl_4^+
$\text{Zr}-\text{Cl}$ distance ($\text{\AA}$)	2.37	2.38	2.35	2.34 (2.336)	2.29	2.30	2.32	2.36
Bond angle ($^\circ$)	180	135.9	120	109	180	110	120	109
HOMO–LUMO gap (eV)	0.46	3.84	3.53	4.35	3.98	3.44	3.21	4.39
Charge transfer from Zr to Cl (e)	0.47	0.47	0.43	0.36	0.26	0.23	0.21	0.13

The EI-MS measurements provide a clear evidence of monochloride, dichloride, trichloride in the gas phase which are due to the fragmentation of ZrCl_4 . The absence of Zr_2Cl_7^+ in the gas phase might be due to the instability of this species in our experimental conditions. Therefore, the dissociation scenario of ZrCl_4 into the lower chloride species has been investigated as follows.

- (1) $2\text{ZrCl}_4 \rightarrow 2\text{ZrCl}_3 + \text{Cl}_2$, $\Delta E = 3.44$ eV/Cl;
- (2) $2\text{ZrCl}_4 \rightarrow 2\text{ZrCl}_2 + 2\text{Cl}_2$, $\Delta E = 3.71$ eV/Cl;
- (3) $2\text{ZrCl}_4 \rightarrow 2\text{ZrCl} + 3\text{Cl}_2$, $\Delta E = 3.81$ eV/Cl.

It is found that the dissociation cost of ZrCl_4 to ZrCl_3 is ~ 3.44 eV/Cl while the dissociation cost to produce ZrCl_2 and ZrCl are, respectively, 3.71 and 3.81 eV/Cl. These results indicate that the formation of ZrCl and ZrCl_2 are the most energetically expensive and that those species are not as abundant as ZrCl_3 in the gas phase.

4 Conclusions

In summary, ZrCl_4 was synthesized from the thermal reaction between zirconium metal and chlorine gas and analyzed by EI-MS. The EI-MS results indicate the presence of ZrCl_4^+ , ZrCl_3^+ , ZrCl_2^+ and ZrCl^+ in the gas phase. The abundance of ZrCl_4 fragments in the gas phase follow the order $\text{ZrCl}_3^+ \gg \text{ZrCl}_2^+ \sim \text{ZrCl}^+$. Previously reported dimeric species (i.e., Zr_2Cl_7) [18] have not been observed in our experimental conditions.

The structure and energetics of neutral and ionic ZrCl_x ($x = 1, 2, 3, 4$) in the gas phase were investigated by DFT methods. The studies of both neutral and ionic species are of interest in the zirconium cladding purification process to explain the formation of ternary compounds, such as ZrFeCl_6 [19], observed in the gas phase. The process by which these intermediate ternary compounds are formed is not well understood, and it could involve both neutral and ionic forms of the chlorides due to molecular collisions at high temperatures. The calculated structural parameters are well in agreement with the one found in the literature. Calculations indicate the energy cost to produce ZrCl_2 and ZrCl fragments is higher than the one to produce ZrCl_3 which gives a rational explanation to the large abundance of ZrCl_3 in the gas phase during EI-MS. The high stability of ZrCl_3 in the gas phase indicates that this species could be used in volatility based separation of Zr cladding. For example, the Zr cladding could be initially chlorinated, the resulting chloride species (ZrCl_4 , metal chloride impurity) would be reduced with hydrogen and the resulting ZrCl_3 separated from the chloride impurity after thermal treatment. Similarly, ZrCl_3 could be the species that reacts with FeCl_3 to form dimeric species, and therefore making iron a

difficult impurity to remove. Current works are in progress in our laboratory to develop a process based on purification of Zr cladding involving ZrCl_3 .

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Homerin G, Baudelet D, Dufrénoy P, Rigo B, Lipka E, Dezitter X, Furman C, Millet R, Ghinet A (2016) ZrCl_4 as a new catalyst for ester amidation: an efficient synthesis of h-P2X7R antagonists. *Tetrahedron Lett* 57:1165–1170
2. Lustman B, Kerze JF (1955) The metallurgy of zirconium. Mc Graw Hill, New York
3. Van der Vis MGM, Cordfunke EHP, Konings RJM (1997) Thermochemical properties of zirconium halides: a review. *Thermochim Acta* 302:93–108
4. Bohe AE, Andrade Gamboa JJ, Pasquevich DM (1997) Chlorination process applied to zirconium recovery from zircaloy shavings. *Mater Sci Technol* 13(10):865–871
5. Collins ED, DelCul GD, Spencer BB, Brunson RR, Johnson JA, Terekhov DS, Emmanuel NV (2012) Process development studies for zirconium recovery/recycle from used nuclear fuel cladding. *Procedia Chem* 7:72–76
6. Ogawa T, Fukuda K, Kashimura S, Tobita T, Kobayashi F, Kado S, Miyayoshi H, Takahashi I, Kikuchi T (1992) Performance of ZrC-coated particle fuel in irradiation and postirradiation heating tests. *J Am Ceram Soc* 75(11):2985–2990
7. Weck PF, Kim E, Tikare V, Mitchell JA (2015) Mechanical properties of zirconium alloys and zirconium hydrides predicted from density functional perturbation theory. *Dalton Trans* 44:18769–18779
8. Kim E, Weck PF, Borjas R, Poineau F (2018) Lattice dynamics and thermomechanical properties of zirconium(IV) chloride: evidence for low-temperature negative thermal expansion. *Chem Phys Lett* 691:98–102
9. Borjas Nevarez R, Mariappan Balasekaran S, Kim E, Weck PF, Poineau F (2018) Zirconium tetrachloride revisited. *Acta Crystallogr C* 74(3):307–311
10. Spiridonov VP, Akishin PA, Tsirel'nikov VI (1962) Electronographic investigation of the structure of zirconium and hafnium tetrachloride molecules in the gas phase. *Zh Strukt Khim* 3(3):329–330
11. Barnes C, Kandziolka M, Ortiz M, McAnly E, DelCul GD, McLaughlin DF (2016) Investigations into the gas phase reactions of zirconium tetrachloride (ZrCl_4) from UNF cladding. *Trans Am Nucl Soc* 114:203

12. Liu C, Liu B, Shao Y, Li Z, Tang C (2008) Vapor pressure and thermochemical properties of $ZrCl_4$ for ZrC coating of coated fuel particles. *Trans Nonferr Met Soc China* 18:728–732
13. Pershina V, Borschevsky A, Illias M, Turler A (2014) Theoretical predictions of properties and volatility of chlorides and oxychlorides of group-4 elements. II. Adsorption of tetrachlorides and oxydichlorides of Zr, Hf, and Rf on neutral and modified surfaces. *J Chem Phys* 1:1. <https://doi.org/10.1063/1.4891531>
14. Sahan Thanthiriwatte K, Vasiliu M, Battey SR, Lu Q, Peterson KA, Andrews L, Dixon DA (2015) Gas phase properties of MX_2 and MX_4 ($X = F, Cl$) for $M =$ group 4, group 14, cerium, and thorium. DOI, *J Phys Chem A*. <https://doi.org/10.1021/acs.jpca.5b02544>
15. Delley B (2000) From molecules to solids with the DMol³ approach. *J Chem Phys*. <https://doi.org/10.1063/1.1316015>
16. Perdew JP, Wang Y (1992) Accurate and simple analytic representation of the electron-gas correlation energy. *Phys Rev B* 45:13244
17. Kirihaara T, Nakagawa I, Seki Y, Honda Y, Ichihara Y (1989) Separation of hafnium tetrachloride from zirconium tetrachloride. *FR* 2625739, A1
18. Schäfer H, Binnewies M (1974) Die Stabilität gasformiger dimerer Chloridmolekeln. *Z Anorg Allg Chem* 410:251–268
19. Troyanov SI, Kharisov BI, Berdonosov SS (1992) Crystal structure of $FeZrCl_6$ —a new structural type for ABX_6 compounds. *Zh Neorg Khim* 37:2424–2429

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