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**Formation and Stability of gaseous WS₂Cl₂, WS₂Br₂ und
WS₂I₂**

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3 **Formation and Stability of gaseous WS₂Cl₂, WS₂Br₂ and WS₂I₂,**
4 **- a combined experimental and theoretical study**
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11 Dedicated on the occasion of the 65. birthday of Rüdiger Kniep
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Keywords

mass spectrometry, ab initio calculation, thermodynamic, tungsten, sulfidehalide

Abstract Gaseous WS_2Cl_2 and WS_2Br_2 are formed by the reaction of solid WS_2 with chlorine resp. bromine at temperatures of about 1000 K. This could be shown by mass spectrometric measurements. The heats of formation and entropies of WS_2Cl_2 and WS_2Br_2 have been determined by means of mass spectrometry (MS) and quantum chemical calculations (QC). WS_2I_2 could not be detected by experimental methods. This is in line with the quantum chemically determined equilibrium constant of the formation reaction.

The following values are given:

$$\Delta_f H_{298}^0(\text{WS}_2\text{Cl}_2) = -230.8 \text{ kJ}\cdot\text{mol}^{-1} \text{ (MS)}, \Delta_f H_{298}^0(\text{WS}_2\text{Cl}_2) = -235.0 \text{ kJ}\cdot\text{mol}^{-1} \text{ (QC)},$$

$$S_{298}^0(\text{WS}_2\text{Cl}_2) = 370.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ (QC) and}$$

$$c_p^0 T(\text{WS}_2\text{Cl}_2) = 103.78 + 7.07\cdot 10^{-3} T + -0.93\cdot 10^5 T^2 + -3.25\cdot 10^{-6} T^2 \text{ (298.15 K} < T < 1000 \text{ K) (QC)}.$$

$$\Delta_f H_{298}^0(\text{WS}_2\text{Br}_2) = -141.9 \text{ kJ}\cdot\text{mol}^{-1} \text{ (MS)}, \Delta_f H_{298}^0(\text{WS}_2\text{Br}_2) = -131.5 \text{ kJ}\cdot\text{mol}^{-1} \text{ (QC)},$$

$$S_{298}^0(\text{WS}_2\text{Br}_2) = 393.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ (QC) and}$$

$$c_p^0 T(\text{WS}_2\text{Br}_2) = 104.84 + 5.32\cdot 10^{-3} T + -0.75\cdot 10^5 T^2 + -2.45\cdot 10^{-6} T^2 \text{ (298.15 K} < T < 1000 \text{ K) (QC)}.$$

$$\Delta_f H_{298}^0(\text{WS}_2\text{I}_2) = -18.0 \text{ kJ}\cdot\text{mol}^{-1} \text{ (QC)}, S_{298}^0(\text{WS}_2\text{I}_2) = 409.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ (QC) and}$$

$$c_p^0 T(\text{WS}_2\text{I}_2) = 105.17 + 4.77\cdot 10^{-3} T + -0.67\cdot 10^5 T^2 + -2.19\cdot 10^{-6} T^2 \text{ (298.15 K} < T < 1000 \text{ K) (QC)}.$$

These molecules have the expected C_{2v} -symmetry.

1 Introduction

Whereas oxidehalides of tungsten have intensively been investigated due to their paramount importance on the mass transport inside halogen lamps, there are almost much less literature data available on the homologous sulfidehalides and selenidehalides. NGAI and STAFFORD [1] reported in 1971 a manuscript in preparation by SINGLETON that obviously has never been published. It was intended to provide mass spectrometric data on gaseous WS_2Cl_2 and $WSOCl_2$. Detailed information on these species is not given in [1]. But SINGLETON and Stafford have published in 1972 a mass spectrometric study of some transition metaloxide- and sulfidehalides [2]. In this paper solid $WScI_4$ has been evaporated at 68 °C and the vapour above this solid was analyzed by means of mass spectrometry to consist of $WScI_4$ -molecules. Up to now no informations about the thermodynamic stabilities of tungstensulfidehalides are available. In the course of an in-depth investigation on the formation and stability of gaseous sulfide- and selenidehalides of tungsten, we studied the reaction of solid WS_2 with chlorine, bromine as well as iodine by means of high temperature mass spectrometry. We found that at a temperature of 1000 K WS_2Cl_2 and WS_2Br_2 but not WS_2I_2 are formed. Probably a small part of $WScI_4$ is formed in the case of chlorine. Molecules like these may play an important role in the chemical vapor transport of tungsten sulfides. Here we report on the formation, thermodynamic data and molecular structures of these sulfidehalides.

2 Results and discussion

The molecules WS_2Cl_2 and WS_2Br_2 have been detected as reaction products formed during the reaction of solid WS_2 with the gaseous halogens. WS_2I_2 could not be detected this way. These molecules have been structurally characterized by means of quantum chemical methods. Thermodynamic data have been determined both by means of mass spectrometry (WS_2Cl_2 and WS_2Br_2) and quantum chemical calculations (WS_2Cl_2 , WS_2Br_2 and WS_2I_2).

2.1 Mass spectrometric investigation

WS_2Cl_2 : The reaction of solid tungsten(IV)-sulfide with gaseous chlorine has been followed by high temperature mass spectrometry at 750 °C. As the main reaction product, gaseous WS_2Cl_2 is formed almost quantitatively according to reaction (1):



We recorded the following mass spectrum at 750 °C (MAT 212, EI, 70 eV, rel. int/%. in ()), In figure 1 the schematic mass spectrum is given. Each bar represents a complicated isotopic pattern. As an example the observed pattern of WS_2Cl_2^+ is shown in comparison with the calculated ones of WS_2Cl_2 and WScCl_3 in figure 2.

Mass spectrum: Cl^+ (5.2), HCl^+ (28.7), S_2^+ (4), Cl_2^+ (0.6), W^+ (2,9), WS^+ (12), WCl^+ (6.4), WS_2^+ (7,9), WScCl^+ (17.8), WCl_2^+ (6), WS_2Cl^+ (35.5), WScCl_2^+ (30.1), WSOCl_2^+ (4.6), WS_2Cl_2^+ (100), WScCl_3^+ (<5)?.

These ions were identified according to their mass numbers and their very characteristic isotopic patterns. We attribute Cl_2^+ to the Cl_2 -molecule and all tungsten containing ions to WS_2Cl_2 . The observed isotopic pattern of WS_2Cl_2^+ deviates a little bit from the calculated one: the intensity of the signals observed at $m/z = 323$ and 325 are a little bit higher than expected. This is probably due to a small contribution of less than 5 % of WScCl_3^+ as reported by Singleton (see figure 2) [2]. Because the intensity of the ion WScCl_3^+ , generated by fragmentation of WScCl_4 is much more higher than the intensities of the other fragments of WScCl_4 their contribution to the peaks observed in this study is negligible. The origin of Cl^+ is unclear as it may be due the fragmentation of Cl_2 , HCl and/or WS_2Cl_2 . Therefore Cl^+ remains unconsidered in the quantitative analysis of the mass spectrum. WSOCl_2 is obviously formed due to the presence of traces of oxygen or water. Because of its low amount it will not be considered in the analysis of the spectrum. To gain quantitative information on the fractions of $\text{Cl}_2(\text{g})$ and $\text{WS}_2\text{Cl}_2(\text{g})$ in the gas phase and to obtain data on the thermodynamic stability of $\text{WS}_2\text{Cl}_2(\text{g})$, we use the approximate equation (2) in which the intensities of the ions measured by mass spectrometry are linked to their partial pressures. Different ionization efficiencies and secondary electron yields at the multiplier are not taken into account.

$$p_i = c \cdot \sum I_i \cdot T \quad (2)$$

p_i : partial pressure of gas phase species i

c : proportionality factor

$\sum I_i$: sum of all intensities of i

T : reaction temperature

The equilibrium constant $K_p(1)$ is expressed as

$$K_p(1) = \frac{p(\text{WS}_2\text{Cl}_2)}{p(\text{Cl}_2)} = \frac{c \cdot \sum I(\text{WS}_2\text{Cl}_2) \cdot T}{c \cdot \sum I(\text{Cl}_2) \cdot T} = \frac{\sum I(\text{WS}_2\text{Cl}_2)}{\sum I(\text{Cl}_2)} \quad (3)$$

In this case of a reaction without change of number of moles (1) the proportionality factor as well as the temperature may be cancelled, the equilibrium constant is expressed by the fraction of the sums of the intensities (3). To determine the reaction enthalpy by means of the “third law” method, it is necessary to take the reaction entropy of (1) into account. A reliable estimation is provided by reaction (4) from which thermodynamic data are well known [3]:



50.5	223.1	354.1	$S_{298}^0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [3]
133.8	266.8	472.4	$S_{1000}^0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [3]
-589.7	0	-671.5	$\Delta H_{298}^0 / \text{kJ} \cdot \text{mol}^{-1}$ [3]
-539.9	25.6	-601.7	$\Delta H_{1000}^0 / \text{kJ} \cdot \text{mol}^{-1}$ [3]

The reaction entropies of (1) and (4) are expected to be very similar. The same is true for the differences ($\Delta_R S_{1000}^0 - \Delta_R S_{298}^0$) and ($\Delta_R H_{1000}^0 - \Delta_R H_{298}^0$). From literature data [3] the following values are necessary for the analysis of reaction (1); i.e. $\Delta_R S_{1000}^0(4) = 71.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Delta_R S_{298}^0(4) = 80.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Delta_R H_{1000}^0(4) = -87.4 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_R H_{298}^0(4) = -81.8 \text{ kJ} \cdot \text{mol}^{-1}$. Taking into account the standard entropies of $\text{WS}_2(\text{s})$ and $\text{Cl}_2(\text{g})$ [3] the following value for the entropy of WS_2Cl_2 is calculated:

$$S_{298}^0(\text{WS}_2\text{Cl}_2(\text{g})) = 368.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

From the experimentally determined equilibrium constant $K_p(1)$, the reaction enthalpies $\Delta_R H_{1000}^0(1)$ as well as $\Delta_R H_{298}^0(1)$ are computed by means of the van 't Hoff isochore (5).

$$\Delta_R H_{T(1)}^0 = -R \cdot T \cdot \ln K(1) + T \cdot \Delta_R S_{T(4)}^0 \quad (5)$$

Based on the analysis of the intensities and the attribution of the ions to the reacting species from the mass spectrum measured at 750 °C, an equilibrium constant $K_p(1) = 379$ is calculated, leading to values of the reaction enthalpy of (1) to be $\Delta_R H^0_{1023}(1) = 23 \text{ kJ}\cdot\text{mol}^{-1}$ or $\Delta_R H^0_{298}(1) = 28.6 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. Using help of $\Delta_f H^0_{298}(\text{WS}_2(\text{s})) = -259.4 \text{ kJ}\cdot\text{mol}^{-1}$ [3], the standard heat of formation of gaseous WS_2Cl_2 is derived:

$$\Delta_f H^0_{298}(\text{WS}_2\text{Cl}_2(\text{g})) = -230.8 \text{ kJ}\cdot\text{mol}^{-1}.$$

WS₂Br₂: The reaction of solid tungsten(IV)-sulfide with gaseous bromine has been followed at 750 °C in the same way as described above. As the only reaction product, gaseous WS_2Br_2 is formed according to reaction (6):



As an example we recorded the following mass spectrum at 750 °C (MAT 212, EI, 70 eV, rel. int/%. in ()): Br^+ (100), Br_2^+ (72,5), W^+ (1,2), WS^+ (2,2), WS_2^+ (1,9), WSBr^+ (2,6), WS_2Br^+ (6,9), WSBr_2^+ (2,9), WS_2Br_2^+ (9,7). We attribute Br_2^+ to Br_2 and all tungsten containing ions to the molecule WS_2Br_2 . WSBr_3^+ as the expected most intensive fragment of WSBr_4 could not be observed. The origin of Br^+ is unclear; it may be due the fragmentation of Br or Br_2 . From this reason we have recorded the mass spectrum of bromine at room temperature. The relative intensity of Br^+ was very low. Therefore, the formation of Br^+ , observed at 750 °C, is mostly due to the ionisation of bromine atoms. The quantitative evaluation of the intensities in the mass spectrum has been done in the same way as described for reaction (1).

Taking into account the standard entropies of $\text{WS}_2(\text{s})$ and $\text{Br}_2(\text{g})$ [3] the following value is calculated:

$$S^0_{298}(\text{WS}_2\text{Br}_2(\text{g})) = 390.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

From the experimentally determined equilibrium constant $K_p(6)$, the reaction enthalpies $\Delta_R H^0_{1000}(1)$ as well as $\Delta_R H^0_{298}(1)$ are computed by means of the van't Hoff isochore (5). Based on the analysis of 10 mass spectra in the temperature range between 600 and 750 °C we have calculated the following values for $\Delta_R H^0_{1000}(6)$: 81.7, 81.8, 81.8, 76.0, 80.8, 83.3, 77.5, 76.5, 86.7, 83.9 $\text{kJ}\cdot\text{mol}^{-1}$, mean value 81.0 $\text{kJ}\cdot\text{mol}^{-1}$ or $\Delta_R H^0_{298}(6) = 86.6 \text{ kJ}\cdot\text{mol}^{-1}$,

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3 respectively. Using the help of $\Delta_f H^0_{298}(\text{WS}_2(\text{s})) = -259.4 \text{ kJ}\cdot\text{mol}^{-1}$ [3] and $\Delta_f H^0_{298}(\text{Br}_2(\text{g})) =$
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5 $30.9 \text{ kJ}\cdot\text{mol}^{-1}$ [3], the standard heat of formation of gaseous WS_2Br_2 is derived:

$$\Delta_f H^0_{298}(\text{WS}_2\text{Br}_2(\text{g})) = -141.9 \text{ kJ}\cdot\text{mol}^{-1}$$

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11 We assume that the accuracy of the determination of the equilibrium constants is at most ± 200
12 % leading to an uncertainty of $\Delta_R H^0(1)$ of about $\pm 12 \text{ kJ}\cdot\text{mol}^{-1}$. From an uncertainty of ± 5
13 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ with respect to the reaction entropy, an error on the enthalpy of formation of
14 gaseous $\text{WS}_2\text{Cl}_2(\text{g})$ and $\text{WS}_2\text{Br}_2(\text{g})$ of about $\pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ results. Therefore the given value
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16 should not deviate more than $17 \text{ kJ}\cdot\text{mol}^{-1}$ from the true value.
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23 **WS₂I₂:** During the reaction of solid WS_2 with gaseous iodine we could not observe a
24 tungstensulfideiodide in the gas phase. This means that the equilibrium constant K_p for
25 reaction (7) must be lower than 10^{-4} .
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30 31 32 33 34 35 **2.2 Quantum chemical calculations**

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37 Theoretical values of the standard heat of formation and the entropy of gaseous WS_2X_2 ($\text{X} =$
38 Cl, Br, I) were obtained by means of the theoretical investigation of the following reaction:
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47 The geometries and energies of the molecules under discussion were calculated on the RI-
48 MP2 level ([4], basis sets of def2-QZVPP quality [5 - 8], 28 and 60 electron pseudo potential
49 for iodine and tungsten, respectively). All the calculations entailed the use of the
50 TURBOMOLE package [9]. The high quality of this procedure for the theoretical calculation
51 of thermodynamic data has been proven before [10, 11]. The electronic structure of WS_2X_2
52 was calculated restricted to symmetry C_{2v} . MP2 frequencies were obtained by diagonalization
53 of the numerically computed Hessian using the module NumForce.
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59 After determination of the theoretical vibrational spectra (WS_2Cl_2 : irreducible representation
60 a_1 : 110.1, 183.3, 404.8, a_2 : 142.8, b_1 : 139.5, 419.6, b_2 : 132.4, 545.8 cm^{-1} ; WS_2Br_2 : a_1 : 73.7,
177.7, 260.0, 532.7; a_2 : 122.8; b_1 : 130.0, 282.9; b_2 : 110.0, 528.5 cm^{-1} ; WS_2I_2 : a_1 : 56.2, 165.4,

217.1, 512.4; a_2 : 109.6; b_1 : 113.8, 240.1; b_2 : 91.0, 532.9 cm^{-1}) of the molecules, their temperature dependent molar heat capacities, entropies, internal energies and its zero point energies were calculated using procedures of statistical thermodynamics (module FREEH). The standard heats of formation $\Delta_f H^0_{298}(\text{WS}_2\text{X}_2, \text{calc.})$ were derived taking into account the theoretically computed reaction enthalpies $\Delta_R H^0_{298}(8, \text{calc.})$ (differences of the electronic energies corrected by thermal energies and the zero point energies, table 1: WS_2Cl_2 : -307.9, WS_2Br_2 : -298.3, WS_2I_2 : -282.3 kJ mol^{-1}) and the well known experimental values for the heats of formation of O_2 , S_2 and WO_2X_2 [12]:

$$\Delta_f H^0_{298}(\text{WS}_2\text{X}_2, \text{calc.}) = -\Delta_R H^0_{298}(\text{calc.}) + \Delta_f H^0_{298}(\text{WO}_2\text{X}_2, \text{exp. [3, 12]}) + \Delta_f H^0_{298}(\text{S}_2, \text{exp. [12]}).$$

By means of this procedure the following theoretical thermodynamic values of WS_2X_2 are obtained:

$$\Delta_f H^0_{298}(\text{WS}_2\text{Cl}_2(\text{MP2})) = -235.0 \text{ kJ}\cdot\text{mol}^{-1} \text{ and } S^0_{298}(\text{WS}_2\text{Cl}_2(\text{MP2})) = 370.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$\Delta_f H^0_{298}(\text{WS}_2\text{Br}_2(\text{MP2})) = -131.5 \text{ kJ}\cdot\text{mol}^{-1} \text{ and } S^0_{298}(\text{WS}_2\text{Br}_2(\text{MP2})) = 393.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$\Delta_f H^0_{298}(\text{WS}_2\text{I}_2(\text{MP2})) = -18.0 \text{ kJ}\cdot\text{mol}^{-1} \text{ and } S^0_{298}(\text{WS}_2\text{I}_2(\text{MP2})) = 409.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

The theoretical values of WS_2Cl_2 and WS_2Br_2 are in excellent agreement with the experimental data. They perfectly confirm that the mass spectrum resulting from the reaction of solid WS_2 with gaseous Cl_2 as well as Br_2 is due to the gaseous high temperature species WS_2Cl_2 and WS_2Br_2 (figure 3).

The temperature dependence of the heat capacities $c_p^0_T$ is usually expressed by the following polynome:

$$c_p^0_T = a + b \cdot 10^{-3} T + c \cdot 10^5 T^2 + d \cdot 10^{-6} T^4 \quad (298.15 \text{ K} < T < 1000 \text{ K}).$$

The coefficients were calculated by the mathematical program package MAPLE [13] choosing four values of $c_p^0_T$ ($T = 298.15, 532.1, 766.05, 1000 \text{ K}$) as given from the FREEH module (table 2). Accurate values for the heat of formation and the entropy at different temperatures can be obtained using Kirchhoff's law.

From the mass spectrometric investigation of the reaction



the expected product $\text{WS}_2\text{I}_2(\text{g})$ is not observed. This experimental finding is in line with the very low calculated equilibrium constant $K_{p,1000}(9) = 10^{-5}$ of the reaction obtained by means of $\Delta_f H^0_{298}(\text{WS}_2\text{I}_2(\text{MP2}))$.

2.3 Discussion

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3 In table 2 the sets of thermodynamic data of WS_2Cl_2 , WS_2Br_2 and WS_2I_2 are tabularized. In
4 order to compare enthalpy-values of different molecules with each other it is better to
5 compare the *heats of atomization* because these values are free from special properties of the
6 elements in their standard states (table 3). The heat of atomization of a gaseous compound is
7 equal to the sum of all bond enthalpies in the molecule under discussion. The values show
8 clearly, that, as expected, the oxidehalides are more stable than the sulfidehalides. But the
9 differences between the heats of atomization of $\text{WO}_2\text{Cl}_2/\text{WS}_2\text{Cl}_2$, $\text{WO}_2\text{Br}_2/\text{WS}_2\text{Br}_2$ and
10 $\text{WO}_2\text{I}_2/\text{WS}_2\text{I}_2$ differ strongly from each other. The difference, between WO_2Cl_2 and WS_2Cl_2 is
11 the biggest one ($382.9 \text{ kJ}\cdot\text{mol}^{-1}$), the differences between $\text{WO}_2\text{Br}_2/\text{WS}_2\text{Br}_2$ and $\text{WO}_2\text{I}_2/\text{WS}_2\text{I}_2$
12 are significantly lower (370.5 , $355.3 \text{ kJ}\cdot\text{mol}^{-1}$). Obviously is the bonding of a tungsten atom to
13 oxygen and chlorine in a special kind favoured. These examples show the difficulties of
14 estimation of heats of formation using bond energy increments. A carefully performed
15 quantum chemical calculation is usually better than any kind of estimation.
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26 Our study has shown that at high temperatures molecules of the type WS_2X_2 are
27 favoured compared with WSX_4 .
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31 **3 Experimental**

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35 The mass spectrometric measurements were performed with a modified mass spectrometer
36 MAT 212 (Finnigan MAT). The gas phase molecules were ionized by electron impact. The
37 reaction of WS_2 with Cl_2 was conducted in a double Knudsen cell. In the front part of the
38 Knudsen cell WS_2 was heated to $750 \text{ }^\circ\text{C}$, in the back part solid copper(II)-chloride that
39 decomposed to copper(I)chloride served as Cl_2 source. Bromine and Iodine have been
40 evaporated outside the vacuum system of the mass spectrometer and then lead into the
41 Knudsen cell. The total pressure in the Knudsen cell was estimated to be around 10^{-5} mbar.
42 The experimental setup was described elsewhere [14]. WS_2 , Aldrich, powder $2 \mu\text{m}$, 99%.
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Table 1: Total energies E_{tot} , thermal energies ΔU^0_{298} , standard heats of formation $\Delta_f H^0_{298}$ as well as entropies S^0_{298} of O_2 , S_2 , WO_2X_2 and WS_2X_2 (X= Cl, Br, I).

	MP2/def2-QZVPP			
	E_{tot} (a.u.)	ΔU^0_{298} (kJ·mol ⁻¹)	$\Delta_f H^0_{298}$ (kJ·mol ⁻¹)	S^0_{298} (J·K ⁻¹ mol ⁻¹)
O_2 ($^3\Sigma_g^-$)	-150.156012	15.07	0	205.1 [12]
S_2 ($^3\Sigma_g^-$)	-795.449964	10.82	128.6 [12]	228.2 [12]
WS_2Cl_2 ($^1\Sigma_g^+$)	-1782.064740	34.27	-235.0 [12]	370.7 [12]
WO_2Cl_2 ($^1\Sigma_g^+$)	-1136.888278	39.10	-671.5 [12]	353.9 [12]
WS_2Br_2 ($^1\Sigma_g^+$)	-6007.89156	33.30	-131.5 [MP2]	393.9 [MP2]
WO_2Br_2 ($^1\Sigma_g^+$)	-5362.711400	38.04	-558.4 [12]	368.4 [12]
WS_2I_2 ($^1\Sigma_g^+$)	-1457.262239	32.93	-18.0 [MP2]	409.9 [MP2]
WO_2I_2 ($^1\Sigma_g^+$)	-812.075940	37.57	-428.9 [12]	377.1 [12]

Table 2: Thermodynamic data of tungsten sulfidehalides

compound	$\Delta_f H_{298}^0$	$\Delta_{at} H_{298}^0$	S_{298}^0	$c_p^0 T = a + b \cdot 10^{-3} T + c \cdot 10^5 T^2 + d \cdot 10^{-6} T^3$			
	(exp.//theor.) (kJ·mol ⁻¹)	(exp.//theor.) (kJ·mol ⁻¹)	(exp.//theor.) (J·mol ⁻¹ ·K ⁻¹)	(J·mol ⁻¹ ·K ⁻¹)			
				<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
WS ₂ Cl ₂ (g)	-230.8// -235.0	1856.4// 1860.8	-//370.7	103.78	7.07	-0.93	-3.25
WS ₂ Br ₂ (g)	-141.9// -131.5	1748.7// 1738.3	-//393.9	104.84	5.32	-0.75	-2.45
WS ₂ I ₂ (g)	-// -18.0	-//1614.6	-//409.9	105.17	4.77	-0.67	-2.19

Table 3: Comparison of the heats of formation and atomisation of tungsten oxidehalides and tungsten sulfidehalides

	$\Delta_f H^0_{298}$ (mean exp.//theor.)		$\Delta_{at} H^0_{298}$ (mean exp.//theor.)	
WO ₂ Cl ₂ (g)	-671.5 [15]	-671.5//-	2241.5	2241.5//-
WS ₂ Cl ₂ (g)	-232.9	-230.8//-235.0	1858.6	1856.4//1860.8
WO ₂ Br ₂ (g)	-562.8 [12]	-562.8//-	2114.0	2114.0//-
WS ₂ Br ₂ (g)	-136.7	-141.9//-131.5	1743.5	1748.7//1738.3
WO ₂ I ₂ (g)	-428.9 [12]	-428.9//-	1969.9	1969.9//-
WS ₂ I ₂ (g)	-18.0	-//18	1614.6	-//1614.6

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Figure 1: Mass spectrum obtained after reaction of solid WS₂ with gaseous Cl₂.

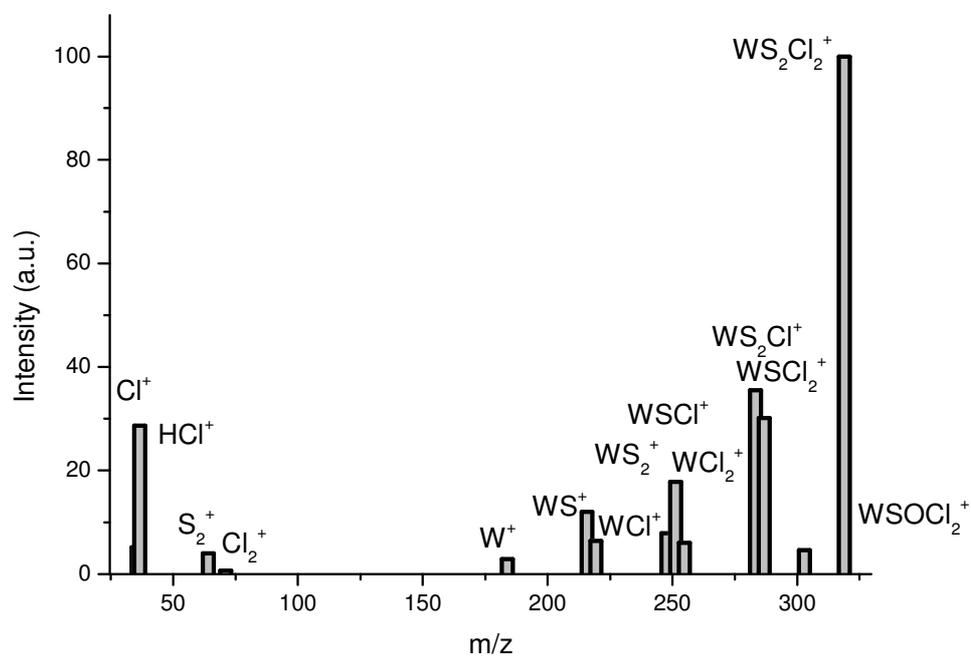
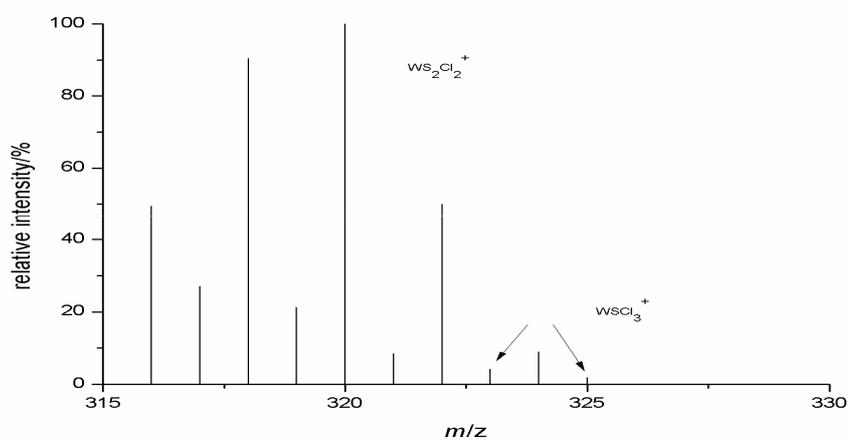
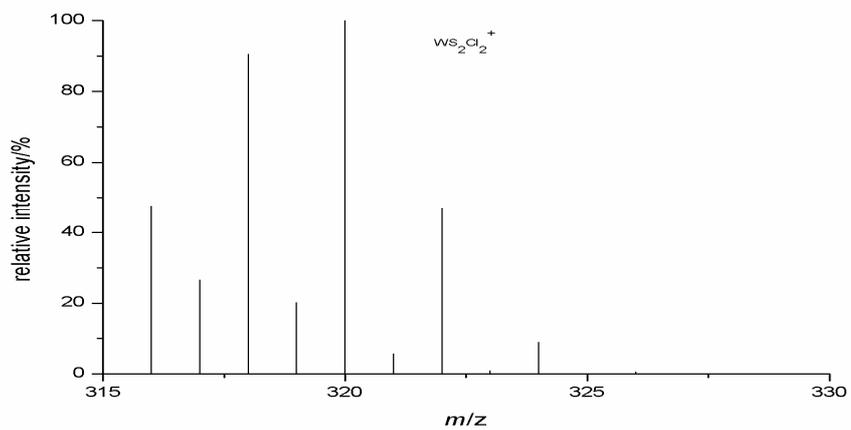


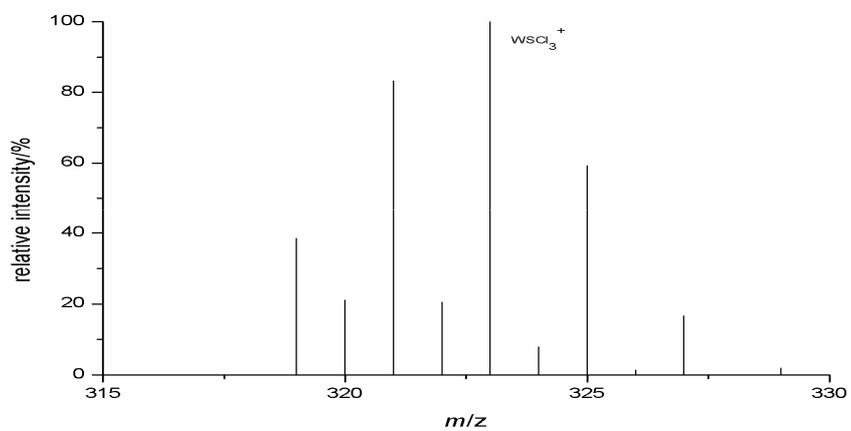
Figure 2: Isotopic patterns: a: observed, b: WS_2Cl_2 (calculated), c: $WScI_3$ (calculated)



a



b



c

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Figure 3: Molecular structures of WS_2X_2 , ($X = Cl, Br, I$) (MP2, distances pm).

