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What is the structure of gas phase CoF_4 ? A thermochemical and spectroscopic approach

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Abstract. In solid state, CoF_4 exhibits a square planar geometry. But, what is its geometry in the gas phase ? By using a thermochemical approach, combining molecular modeling data, as well as experimental data from the literature, it is demonstrated that CoF_4 in the gaseous state most likely exhibits a tetrahedral structure. Based on infrared and thermochemical data, it is also proposed that in gaseous phase (at least in closed systems, such as the Knudsen cell) a chemical equilibrium between both square planar and tetrahedral geometries can be established.

Keywords: CoF_4; gas phase structure; thermochemistry

INTRODUCTION

Thermochemical properties of transition-metal fluorides are of fundamental interest [1]. From the point of view of basic research, the existence of compounds with unusual valence states is of considerable scientific interest, because the achievement of unusual states of oxidation is related to the theories of chemical valence and bonding.

The highest oxidation state of cobalt that has been unambiguously established is V. The tetrafluoride cation $[CoF_4]^+$ has been identified in the gas phase by mass spectrometry in a reaction between CoF_3 and TbF_4 at higher temperatures and this fact also implies the existence of $Co^{IV}F_4$ in the gas phase [2].

In this connection, the thermochemistry of gas phase cobalt fluorides have been investigated experimentally by using Knudsen cell mass spectrometry [3,4].

Solid state CoF_4 is alpha Po structured and crystallizes in the triclinic P1 space group. The structure is zero-dimensional and consists of two CoF_4 clusters. Co^{4+} is bonded in a square co-planar geometry to four equivalent F1-atoms. All Co–F bond lengths are 1.72 Å [5]. By calculations, it has been obtained to CoF_4 the following parameters: a density of 2.81 g/cm^3, an energy band gap of 1.617 eV and the lattice parameters a = b = c = 6.447 Å; $\alpha = \beta = 128.546^\circ$ and $\gamma = 75.742^\circ$ [6].

$CoF_4(g)$ was first detected mass spectrometrically and further mass spectrometric studies [7] provided convincing proof of its existence. Hence, in solid state, CoF_4 exhibits a square planar geometry. But, what is its geometry in the gas phase ?

As will be shown here, by using a thermochemical approach, some interesting insights about the structure of gas phase CoF_4 can be obtained.

METHODOLOGY

The quantum chemical calculations were performed by using Spartan´16 [8]. SE(PM6), approach were employed. The gas phase formation enthalpy was calculated by using the SE-PM6 approach, taking into account its minor computation time consuming and its reliability for calculations involving inorganic systems, including fluorides, as verified for PtF_6 [9], $NH_3.NI_3$ [10] as well as mercury and silver fulminates [11].

The ionization energy was calculated by using the Spartan T1 thermochemical recipe [8].

Density functional (DFT) DFT ωB97X-D/ 6-31G* basis set was employed to calculate the infrared spectra.

CoF_4 was modelled with both: a square planar (1 unpaired electron) and a tetrahedral geometry (5 unpaired electrons). To the tetrahedral structure a high spin configuration was assumed since according to crystal field theory, despite the ligand force field, all tetrahedral compounds must be high spin, due to the fact that $\Delta_t \sim \Delta_{oct}$.

The gas phase experimental values to the formation enthalpy of gas phase CoF_4 are those from literature [3,4].

RESULTS AND DISCUSSION

In 1993, the enthalpy of formation of the gaseous molecule CoF_4 has been reported as -630 ± 30 $kJmol^{-1}$ [3] and in 1997, a recalculated value of -649.0 ± 32.3 $kJmol^{-1}$ was presented [4]. In CoF_4 cobalt is at +4 oxidation state, that is, it exhibits an [Ar] d^5 electron configuration.

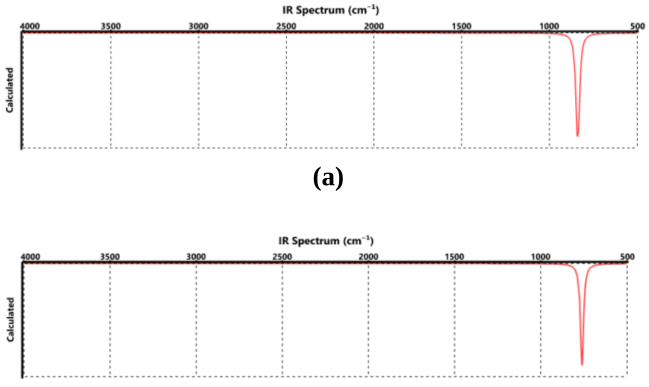
As previously said, CoF_4 was modelled with both: a square planar (1 unpaired electron) and a tetrahedral (5 unpaired electrons) geometry.

For such geometries, the calculated $\Delta H^f(g)$ values are -796.6 $kJmol^{-1}$ and -495.3 $kJmol^{-1}$, respectively, with a mean value of -646.0 $kJmol^{-1}$ in very good agreement with the recalculated experimental value of -649.0 ± 32.3 $kJmol^{-1}$ [4].

It is worth noting that, despite being obtained from experimental data, the enthalpy of formation in the gaseous state for CoF_4 was calculated indirectly, from the enthalpies of formation in gaseous phase of CoF_3 and the enthalpy of the gaseous reaction $CoF_3 + ½\ F_2 \rightarrow CoF_4$ [4]. The enthalpy for reaction $CoF_3 + ½F_2 \rightarrow CoF_4$, in its turn, was previously calculated from standard equilibrium constants by third-law method using the thermodynamic functions for CoF_4, CoF_3 and F_2 [2].

By using MS and FTIR spectroscopy, a study was performed about gaseous cobalt tetrafluoride [7]. From the infrared spectrum of argon-isolated CoF_4 molecules, the Co-F stretching mode has been detected at 767.8 cm^{-1}.

As said earlier, in the present work CoF_4 was modelled with both: a square planar (1 unpaired electron) and a tetrahedral (5 unpaired electrons) geometry. The calculated infrared spectra (DFT ωB97X-D/ 6-31G*) are shown in Figure 1.



(a)

(b)

Figure 1. Calculated (DFT ωB97X-D/ 6-31G*) infrared spectra to square planar (a) and tetraedric (b) gas phase CoF_4.

To the square planar geometry the Co-F stretching mode is a very intense peak at 842 cm^{-1} whereas to the tetraedric geometry, the same stretching mode is located at 763 cm^{-1}, in very good agreement with the 767.8 cm^{-1} experimental value [7]. Hence, based only on the IR spectroscopic data, a tetrahedral structure can be assigned to gaseous CoF_4.

It was verified that the ground state of Co(IV) in CoF_6^{-2} is the low spin $^2T_2$ [12]. Hence, in the present work, CoF_6^{-2} was modelled as octahedral, with one unpaired electron. The $\Delta H^f(g)$ for such complex ion was calculated (SE-PM6) as -1299.8 $kJmol^{-1}$. Subtracting, form this value, 870 $kJmol^{-1}$ (due to breakage of two Co-F bonds = 435 $kJmol^{-1}$ [13]): $CoF_6^{-2}\ (g) \rightarrow CoF_4\ (g) + 2F^-\ (g)$, a value of -429.8 $kJmol^{-1}$ is obtained to the gas phase formation enthalpy of CoF_4 (g) in good agreement with the -495.3 $kJmol^{-1}$ calculated (present work) value to the high spin (tetrahedral) CoF_4(g). Once again, a tetrahedral structure to gaseous CoF_4 is supported. However, why is the $\Delta H^f(g)$ calculated for such structure is so far from the reported experimental value [4] ?

Based on the most recently experimental value to CoF_4 $\Delta H^f(g)$ (-649.0 ± 32.3 $kJmol^{-1}$) [4] and the PM6 mean value calculated in the present work (-646.0 $kJmol^{-1}$), two hypothesis will be discussed: (a) the geometry for gas phase CoF_4 is some kind of distorted one, “intermediary” between square planar (SP) and tetrahedral (T), a “seesaw” geometry, as shown in Figure 2 and (b) in gaseous phase (at least in closed systems, such as the Knudsen cell employed in the cited experiments [3,4]) a chemical equilibrium between both structures is established, as shown in Figure 3.

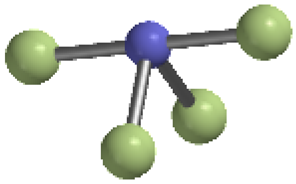


Figure 2. The proposed "intermediary" between square planar (SP) and tetrahedral (T), geometry for gaseous phase CoF_4.

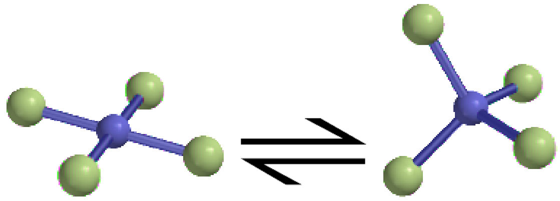


Figure 3. The proposed equilibrium between square planar (SP) and tetraedric (T) structures for gaseous phase CoF_4.

Some remarks are necessary here: in the experiment dedicated to obtain the thermochemical data [4] (direct quote): "The CoF_3 sample was loaded into the platinum effusion cell inside the argon atmosphere dry-box, and evaporated at constant temperature. (…); The X-ray powder diffraction pattern showed the residue to be CoF_2. Ions generated from CoF_4, F_2 molecules and F atoms were searched for in the mass spectrum, but they were not observed during the experiment.". In the FTIR experiment [7]: "The Knudsen effusion mass spectrometry method has been applied to investigate the gas-phase composition over the CoF_3(s)-TbF_4(s) system and to establish the optimum in situ conditions for CoF_4 synthesis. The electron impact mass spectrum of the CoF_4 molecule has been obtained. From the infrared spectrum of argon-isolated CoF_4 molecules, the Co-F stretching mode has been detected at 767.8 cm^{-1}."

Hence, using the authors' own words, we can conclude that a positive identification of the CoF_4 molecules was made in the FTIR experiment, but not in the thermochemical one.

Thus, the thermochemical data obtained in the present study, via molecular modeling, help to consolidate a better understanding of the structure of CoF_4 in the gaseous state.

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