



Computational thermochemistry and a structure for gaseous phase NaCl_3

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Abstract Thermodynamically stable cubic and orthorhombic NaCl_3 as well as NaCl_7 have been synthesized [1]. A thermochemical explanation was recently propose [2] for the stability of such unusual compounds [2]. In the present work, molecular modeling (SE-PM3/MMFF) of a dimmeric structure for NaCl_3 is performed. The calculated cation and anion charges, as well as bond distances for the NaCl_3 gaseous dimmer are in good agreement with values for the solid $Pm3n\text{NaCl}_3$ [1]. To the modelled dimmer $\Delta_f^\circ H^0 = -196.4 \text{ kJmol}^{-1}$. For such dimmeric compound: point group C_1 ; $d_{\text{Na-Na}} = 273.3 \text{ pm}$; $d_{\text{Na-Cl}} = 246.8\text{-}248.1 \text{ pm}$; ZPE 10.01 kJmol^{-1} ; $H^0 = -154.5 \text{ kJmol}^{-1}$; $G^0 = -289.3 \text{ kJmol}^{-1}$, $S^0 = 425.1 \text{ JK}^{-1}\text{mol}^{-1}$; $C_v = 169.6 \text{ JK}^{-1}\text{mol}^{-1}$).

Keywords Gas phase, NaCl_3 , Dimmer, formation enthalpy

Introduction

Thermodynamically stable cubic and orthorhombic NaCl_3 , as well as NaCl_7 and another unusual sodium chlorides have been synthesized [1]. A thermochemical explanation was recently propose for the stability of such unusual compounds [2].

In the present work, molecular modeling is employed to obtain thermochemical data and propose a dimmeric structure for NaCl_3 .

Methodology, Results and Discussion

All computations were performed by using Spartan'14 [3]. To choose an appropriate method/theory level for the computations is, of course, of paramount importance since that predict structures and energetics are the main uses of computational chemistry today [4] and that to know how good is the calculated numbers is an absolute requirement [4].

Before chose a method/theory level for the computations, a "calibration" was performed using NaCl as "standard". Sodium chloride was chose because its obvious relation with the other sodium chlorides. The parameter chose for calibration was dipole moment (μ), since there are reliable experimental values for such parameter for gaseous NaCl and taking into account that μ is the product of charge by distance and so, is obviously related with electrostatic charges and bond distance. Furthermore, as a vectorial parameter, μ values obviously depend on the compound's geometry.

After "screening" a lot of methods/theory levels for the computations, it was chose a Semi-Empirical method (PM3 level of theory; geometry MMFF).

In order to verify the reliability of the chose method, a typical dimmeric compound, AlCl_3 was modelled. A $\Delta_f^\circ H^0$ value of $-1302.2 \text{ kJmol}^{-1}$ was obtained, in very good agreement with the experimental value of $-1295.7 \text{ kJmol}^{-1}$ [5].



Gaseous NaCl has a dipole moment of 9.00 D [5] and a Na-Cl bond distance of 236.1 pm[6]. The chose method gives, for the same parameters, 9.30 D and 232.0 pm. Furthermore, the gaseous phase enthalpy of formation was also used as a “reference” parameter. The calculated thermochemical and structural parameters are summarized in Table 1. The modelled dimmer exhibits a $\Delta_f^\circ H^0$ value of $-196.4 \text{ kJmol}^{-1}$. The calculated value for NaCl, using the same theoretical approach was $-178.94 \text{ kJmol}^{-1}$. As comparison, for NaCl, $\Delta_f^\circ H^0(\text{exp.}) = -181.4 \text{ kJmol}^{-1}$ [7].

Table 1: Thermochemical and structural parameters for the modelled gaseous phase NaCl_3 dimmer (Na_2Cl_6).

Parameter	Gaseous phase dimmer	Solid $Pm3n\text{NaCl}_3$ (Ref. 1)
Point group	C_1	—
μ/D	0.02	—
Cation charge	+0.857	+0.823
Anion charge	-0.286	-0.275
d Na-Na/pm	273.3	—
d Na-Cl/pm	246.8-248.1	230.0
Cl-Na-Cl angle/ $^\circ$	117.72-118.13	—
ZPE/ kJmol^{-1}	10.01	—
$\Delta_f H_g^\circ/\text{kJmol}^{-1}$	-196.4	—
$G^\circ/\text{kJmol}^{-1}$	-289.3	—
$H^\circ/\text{kJmol}^{-1}$	-154.5	—
$S^\circ/\text{JK}^{-1}\text{mol}^{-1}$	425.1	—
$C_v/\text{JK}^{-1}\text{mol}^{-1}$	168.56	—

For the modelled dimmer shown in Figure 1, cation and anion charges of +0.857 and -0.286 were calculated, in very good agreement with the previously obtained for the solid $Pm3n\text{NaCl}_3$ [1]: +0.823 and -0.275, respectively. The positive S° and negative G° and H° values obtained to the modelled NaCl_3 dimmer shows that, from a thermodynamic point of view, such structure is stable.

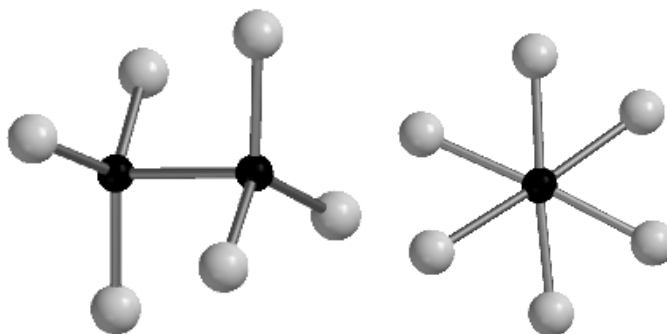


Figure 1: Modelled structure for gaseous NaCl_3 dimer with a Na-Na bond: (a) side view; (b) top view.

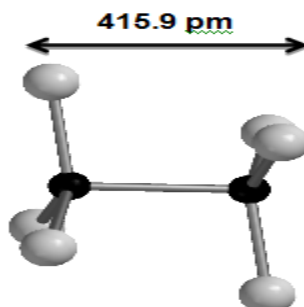


Figure 2: The “length” of the modelled NaCl_3 dimmer



It is worth noting that the dimer's "length" highlighted in Figure 2, is 415.9 pm, whereas in solid $Pm3nNaCl_3$ $a=411.4$ nm [1]. In the dimer, the Na-Cl bond distances range from 246.8 to 248.1 pm, whereas in the solid the nearest Na-Cl distance is 230.0 pm [1]. In the solid, the shortest Cl-Cl distance is 206.0 pm [1]. In the modelled dimer, such distance is 423.7 pm. Such differences could be attributed to the cation-anion interactions between closest ions (present in the solid but absent in the gas phase dimer).

The dimeric structure shown in Figure 1 was proposed based on data for solid $Pm3nNaCl_3$ for which Z (f.u. in the unit cell) = 2[1] as well as on the fact that NaCl can exist as a Na_2Cl_2 dimer in gaseous phase [8]. The infrared spectra for the structure shown in Figure 1 was simulated, and no band in the $4000-500\text{ cm}^{-1}$ range was observed. However, also for gaseous NaCl (both, monomer and dimer) it is verified that all IR bands are in the $370-100\text{ cm}^{-1}$ range [8].

Other hypothetically possible structures were also modelled, with no Na-Na bond, and with bridged chlorine atoms, but none of such structures reproduce the cation and anion charges in good agreement with the solid $Pm3nNaCl_3$ [1]. As the reader certainly noted, it has been assumed here that under melting and subsequent vaporization, the number of formula units in the unit cell (Z) verified to the solid, i.e. 2, is retained. That is, the Cl anions interactions with adjacent Na cations are disrupted as the solid melts and then vaporizes, but the "basic" unit (Na_2Cl_6) is retained.

The solid $Pm3nNaCl_3$ has a lattice volume of 69.63 Å^3 [1] whereas the volume of the modelled dimer is 156.9 Å^3 . Such fact could be explained as follows: whereas the "length" of the dimeric structure is strongly dependant on the Na-Na bond distance, the other two dimensions are strongly affected by the Na-Cl bond distances as well as the Cl-Na-Cl bond angles. In the solid $Pm3nNaCl_3$, the chlorine ions are strongly affected by the surrounding sodium cations, and, consequently, the Na-Cl bonds are shorter than in the gaseous dimer (Table 1), and the Cl-Na-Cl bond angles are, presumably, larger in the gaseous dimer than in the solid. Hence, the gaseous dimer exhibits a higher volume.

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