



# Supersalts $\text{Na}_2\text{AlX}_5$ (X = F, Cl): Quantum Chemical Study of the Structure, Vibration Spectra and Thermodynamic Properties

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## **Authors' contributions**

*This work was carried out in collaboration between all authors. Author EAU performed computations, wrote the first draft of the manuscript and managed literature searches. Author AMP performed some selected computations of thermodynamic properties. Author TPP performed corrections and some selected computations regarding the structure and vibrational spectra. All authors analyzed and discussed the results and approved the final manuscript.*

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## **ABSTRACT**

Theoretical investigation, prediction and design of novel supersalts  $\text{Na}_2\text{AlX}_5$  (X = F, Cl) have been performed. The formation of the supersalts was considered through association reactions between different building blocks: Superalkalies and superhalogens, ionic ( $\text{Na}_2\text{X}^+$  and  $\text{AlX}_4^-$ ), as well as dimers  $\text{Na}_2\text{X}_2$  and traditional salts  $\text{AlX}_3$ . The optimization of geometrical structures, and determination of vibrational spectra of supersalts and their respective building blocks was carried out by the DFT/B3P86 and MP2 methods; The McLean–Chandler basis set and the extended basis set (cc-pVTZ for Na, Al; aug-cc-pVTZ for F, Cl) were used. Different possible geometrical configurations for the supersalts  $\text{Na}_2\text{AlX}_5$  were considered. Consequently, two structures were proved to be isomers: A structure with two cycles in perpendicular planes with a tail ( $C_{2v}$  symmetry) and a compact structure with a tail ( $C_s$  symmetry). Evaluation of their relative concentrations in

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equilibrium vapour was done, and the energies and enthalpies of the association reactions were determined. The enthalpies of formation  $\Delta_f H^\circ(0)$  of gas-phase supersalts are:  $-2250 \pm 45 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\text{Na}_2\text{AlF}_5$ ) and  $-1380 \pm 20 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\text{Na}_2\text{AlCl}_5$ ).

*Keywords: Supersalt; superatom; superhalogen; superalkali; geometrical structure; vibrational spectrum; and enthalpy of formation.*

## 1. INTRODUCTION

The experimental chemist is concerned with observing and, to as great an extent as possible, understanding and interpreting his observation on chemical nature of chemical compounds. In order to formulate experiments imaginatively and interpret them correctly, an understanding of the ideas provided by theory as to behavior of molecules and other arrays of atoms is very essential [1].

The understanding of the properties of elements or compounds serves as the basis for the synthesis of materials. A classic example that demonstrates this principle is the formation of salts. Alkali atoms prefer to give up an electron to become a cation, while halogen atoms prefer to accept an electron to become an anion. In both cases, the outer electrons satisfy the octet rule where the outermost s and p orbitals are full [2].

Salts are ionic chemical compounds useful for domestic purposes, and various technological processes in industries and laboratories. Historically, alkali and alkali earth metals have been used together with halogens to form very stable salts, e.g. NaCl. The alkali cations and halogen anions combine to form a strong ionically bonded compound. This is due to low ionization potential (IP) of metals and high electron affinity (EA) of the halogens.

The proposal on the existence of superatoms by Khanna and Jena [3,4] has diversified the perception of chemists and brought new possibilities and techniques of making chemical species. Superatoms are defined as clusters of atoms with suitable size and composition that can mimic the chemistry of atoms in the periodic table. Superatoms are very important as they provide compounds with novel structures, novel properties and special binding nature which all together contribute to, and promote the development of chemistry [5].

Despite of the enormous progress in the research of superatoms, few attempts have been made in their utilization for designing supersalts,

compounds with unique chemical properties [6]. The recent studies include: Different supersalts by Giri [2], novel  $\text{Li}_3\text{X}_3$  supersalt by Srivastava and Misra [6], and the  $\text{Na}_2\text{MgX}_4$  ( $\text{X} = \text{F}, \text{Cl}$ ) supersalts [7]. Several parameters have been described in these studies including electron affinity, ionization potential, binding energy, vibration spectra and thermodynamic functions but still a critical investigation is needed to be done on these and other properties for different supersalts so as to provide a solid basis for experimentalist and technologist to work on and come out with tangible supersalts having outstanding properties.

Therefore in this article, we have attempted, to design supersalts  $\text{Na}_2\text{AlX}_5$  through three routes using different building blocks: superalkalies and superhalogens, ionic ( $\text{Na}_2\text{X}^+$  and  $\text{AlX}_4^-$ ),  $\text{NaX}$  and  $\text{AlX}_3$  as well as dimers  $\text{Na}_2\text{X}_2$  and traditional salts. The computational results for  $\text{Na}_2\text{X}^+$ ,  $\text{NaX}$  and  $\text{Na}_2\text{X}_2$  used in this study had been taken from [7]. The experimental values for the enthalpies of formation of  $\text{AlX}_4^-$  determined by thermochemical methods are available [8-10]. Second, optimize the geometrical structure of  $\text{Na}_2\text{AlX}_5$  ( $\text{X} = \text{F}, \text{Cl}$ ) supersalts. Third, examine critically the vibrational spectra and thermodynamic properties of supersalts.

## 2. COMPUTATIONAL DETAILS

All calculations have been carried out by using the PC GAMESS program (Firefly 8.1.0 version) [11,12]. Details of the calculations have been described previously [7]. Similarly, the same methods, DFT/B3P86 and MP2, and two basis sets, the first one was McLean–Chandler (MC) with *d*-functions added for all atoms and second cc-pVTZ for metals and aug-cc-pVTZ for halogens denoted hereafter as “Ext” have been used. Geometrical parameters were optimized for the supersalts  $\text{Na}_2\text{AlX}_5$ .

The vibrational analysis was performed at the same level to verify that all obtained structures correspond to a real minima energy by the absence of imaginary frequencies. Geometrical structures were analyzed and examined using

Chemcraft software [13] as a visualization tool. The thermodynamic functions were determined in the rigid rotator-harmonic oscillator approximation using the Open thermo software [14]. The required reference data for the thermodynamic calculations were taken from [15]. The values of enthalpies of reactions  $\Delta_r H^\circ(0)$  were computed theoretically through the total energies ( $\Delta_r E$ ) and zero point vibration energies ( $\Delta_r \epsilon$ ).

### 3. RESULTS AND DISCUSSION

#### 3.1 Analysis of the Computational Approaches for $\text{AlX}_3$ ( $\text{X} = \text{F}, \text{Cl}$ )

Four theoretical approaches B3P86 MC, MP2 MC, B3P86 Ext, MP2 Ext were applied in determining the parameters for  $\text{AlX}_3$ . The computed results for the  $\text{AlX}_3$  molecules are presented in Table 1 and its equilibrium

geometrical structure is given in Fig. 1(a). There is no contradiction between theoretical and available experimental values in terms of internuclear separations, vibrational frequencies and ionization energies obtained by DFT and MP2 methods.

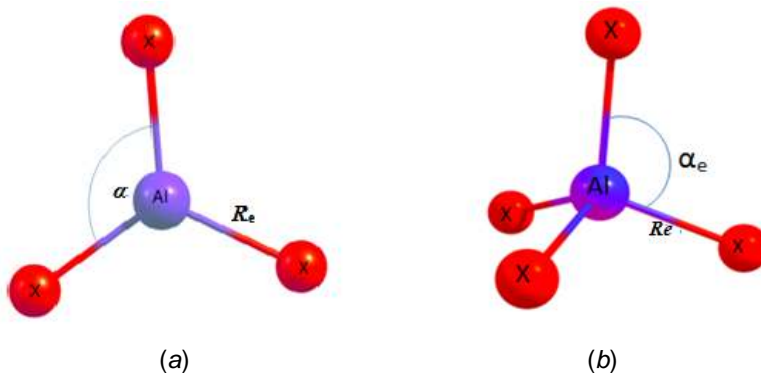
The parameters for  $\text{AlX}_3$  calculated by different methods agree with each other, the difference is within 0.001–0.014 Å for  $R_e$  (Al-X), and about 2% for vibrational frequencies. As compared to the experimental parameters [16–18] the B3P86 Ext and MP2 Ext approaches look preferable.

Earlier [7] the parameters were calculated by similar methods and results were discussed for dimer molecules  $\text{Na}_2\text{F}_2$  and  $\text{Na}_2\text{Cl}_2$ . It was shown also that the results obtained with extended basis sets were in accordance with available reference data.

**Table 1. Comparison of the calculated properties of  $\text{AlX}_3$  ( $\text{X} = \text{F}, \text{Cl}$ ) with the reference data**

Property	B3P86, MC	MP2, MC	B3P86 Ext.	MP2 Ext.	Reference
<b><math>\text{AlF}_3(D_{3h})</math></b>					
$R_e$ , Å	1.648	1.647	1.640	1.640	1.654[16]
$-E$ , a.u.	542.15006	541.52487	542.20754	541.61391	
$IE_{ad}$ , eV	14.24		14.35		15.45[17]
$\omega_1(A_1')$	680	693	680	678	690[16]
$\omega_2(A_2'')$	289	302	294	300	297[16]
$\omega_3(E')$	962(2)	978(2)	944(2)	942(2)	935(2) [16]
$\omega_4(E')$	241(2)	249(2)	243(2)	244(2)	263(2) [16]
<b><math>\text{AlCl}_3(D_{3h})</math></b>					
$R_e$ , Å	2.079	2.066	2.080	2.073	2.060[18]
$-E$ , a.u.	1623.26932	1621.53933	1623.22657	1621.56797	
$IE_{ad}$ , eV	11.52		11.45		12.01[17]
$\omega_1(A_1')$	381	399	375	389	375 [18]
$\omega_2(A_2'')$	198	208	202	206	183 [18]
$\omega_3(E')$	621(2)	647(2)	617(2)	631(2)	595(2) [18]
$\omega_4(E')$	142(2)	150(2)	142(2)	144(2)	150(2) [18]

Notes: Here and hereafter in Tables 2–5,  $R_e$  is the internuclear distance in Å;  $E$  is the total energy in au,  $\mu_e$  is the dipole moment in D;  $IE_{ad}$  is the adiabatic ionization energy, in eV, and  $\omega$  is the fundamental frequency in  $\text{cm}^{-1}$



**Fig. 1. Equilibrium geometrical structures of the species: (a)  $\text{AlX}_3$ ,  $D_{3h}$ ; (b) Ionic superhalogens  $\text{AlX}_4^-$ ,  $T_d$  ( $\text{X} = \text{F}, \text{Cl}$ )**

### 3.2 Geometrical Structure and Vibration Spectra Superhalogens $\text{AlX}_4^- (\text{X}=\text{F}, \text{Cl})$

The equilibrium geometrical structures of the superhalogens;  $\text{AlX}_4^-$  ( $T_d$  symmetry) are presented in Fig. 1 (b). Its geometrical parameters were calculated by B3P86 and MP2 with McLean–Chandler and extended basis set and are shown in Table 2. The geometrical parameters for  $\text{AlX}_4^-$  determined by both methods are in good agreement with the theoretical reference values obtained by MP2/6-311+G(3df) [19].

Generally, both methods produce vibrational frequencies which are in good agreement with the experimental values [20-22] even though results by B3P86 ext method are more preferable. The difference in vibrational frequencies between the two methods for the two salts is  $1\text{-}27\text{ cm}^{-1}$ .

Electronic state of the ionic superhalides for both  $\text{AlX}_4^-$  is  $^1A_1$  and both  $\text{AlF}_4^-$  and  $\text{AlCl}_4^-$  are of  $T_d$  symmetry with an extra electron which is strongly bound. The ionization energies of  $\text{AlX}_4^-$  was determined through HOMO energies by B3P86, MC and Ext. Since  $\text{IE}(\text{AlX}_4^-) = \text{EA}(\text{AlX}_4)$ , the results by B3P86 Ext prove that these molecules are typical superhalogens because much energy is released when they accept electrons. They

have high EA: 5.20 eV ( $\text{AlF}_4^-$ ) and 4.32 eV ( $\text{AlCl}_4^-$ ), as compared to normal halogens, 3.4 eV (F) and 3.6eV (Cl) respectively. Its vibrational frequencies are in good agreement with the available experimental values.

### 3.3 Geometrical Structure and Vibration Spectra of Supersalts $\text{Na}_2\text{AlX}_5$

Two equilibrium geometrical configurations of the  $\text{Na}_2\text{AlX}_5$  molecules have been considered: a structure with two cycles in perpendicular planes with a tail ( $C_{2v}$  symmetry) and a compact structure with a tail ( $C_s$  symmetry). Fig. 2. presents and specifies the optimized geometrical structures of supersalts  $\text{Na}_2\text{AlX}_5$ . Both structures were proved to be in equilibrium as they correspond to the minima at the potential energy surface.

The computed geometrical parameters and fundamental frequencies for  $C_{2v}$  and  $C_s$  structures which was determined by B3P86 and MP2 method with extended basis set are gathered in Tables 3 and 4 respectively. In general there is a good agreement between corresponding geometrical parameters obtained by the two methods. For instance the DFT differs with MP2 internuclear distances  $R_e$  values by  $0.001\text{--}0.065\text{ \AA}$ , bond angle by  $0.0\text{--}2.9^\circ$ , and dipole moment  $\mu_e$  by  $0.08\text{--}0.09\text{ D}$  and fundamental frequencies  $\omega$  by  $0\text{--}35\text{ cm}^{-1}$ .

Table 2. Calculated properties of superhalogens  $\text{AlX}_4^- (\text{X}=\text{F}, \text{Cl})$

Property	B3P86 MC	MP2 MC	B3P86 Ext.	MP2 Ext.	REF.[19]
$\text{AlF}_4^- (T_d)$					
-E	642.21393	641.94625	642.24820	641.57066	
$R_e$	1.706	1.705	1.699	1.698	1.716[19]
IE, eV	3.45		5.20		
$\omega_1$	199(2)	208(2)	192(2)	203(2)	210(2) [20,21]
$\omega_2$	302(3)	313(3)	298(3)	304(3)	322 [20,21]
$\omega_3$	611	623	605	610	622 [20,21]
$\omega_4$	801(3)	815(3)	776(3)	789(3)	760(3) [20,21]
$\text{AlCl}_4^- (T_d)$					
-E	2083.67161	2081.87436	2083.65321	2081.52534	
$R_e$	2.168	2.151	2.168	2.155	2.149[19]
IE, eV	2.79		4.32		
$\omega_1$	113(2)	120(2)	110(2)	114(2)	146(2) [22]
$\omega_2$	175(3)	184(3)	172(3)	173(3)	180(3) [22]
$\omega_3$	336	354	336	348	349 [22]
$\omega_4$	494(3)	521(3)	488(3)	509	490(3) [22]

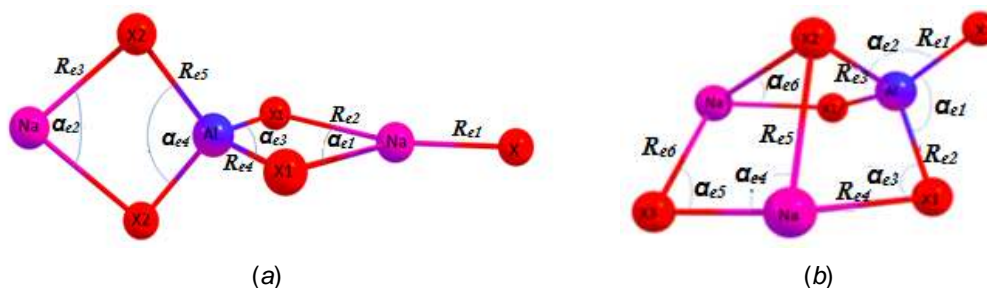


Fig. 2. Equilibrium geometrical configurations of  $\text{Na}_2\text{AlX}_5$ : (a) two-cycled structure ( $C_{2v}$  symmetry) (b) compact structure of  $C_s$  symmetry

Table 3. Calculated properties of supersalts  $\text{Na}_2\text{AlX}_5$  ( $C_{2v}$  symmetry)

Property	$\text{Na}_2\text{AlF}_5$		$\text{Na}_2\text{AlCl}_5$	
	B3P86 ext	MP2ext.	B3P86 ext	MP2ext.
$-E$	1066.72785	1065.22198	2868.49599	2865.21734
Re1 (Na-X)	1.974	1.978	2.421	2.386
Re2 (Na-X1)	2.477	2.405	2.941	2.813
Re3(Na-X2)	2.187	2.172	2.628	2.588
Re4 (Al-X1)	1.676	1.673	2.133	2.123
Re5(Al-X2)	1.718	1.712	2.197	2.180
ae1(X1-Na-X1)	64.3	66.4	72.3	83
ae2(X2-Na-X2)	70.8	71.4	81.1	82.2
ae3(X1-Al-X1)	103.6	103.8	108.8	109.0
ae4(X2-Al-X2)	95.0	95.5	102.2	102.6
$\mu_e$	20.82	21.16	26.71	27.38
$\omega_1$	19	28	12	15
$\omega_2$	32	44	24	17
$\omega_3$	65	83	38	38
$\omega_4$	78	98	56	83
$\omega_5$	80	115	73	96
$\omega_6$	114	132	78	97
$\omega_7$	159	173	100	103
$\omega_8$	199	198	132	136
$\omega_9$	217	231	150	150
$\omega_{10}$	292	300	169	172
$\omega_{11}$	308	311	198	198
$\omega_{12}$	308	314	207	215
$\omega_{13}$	370	371	242	242
$\omega_{14}$	483	483	336	354
$\omega_{15}$	615	623	342	368
$\omega_{16}$	704	723	452	472
$\omega_{17}$	818	833	521	540
$\omega_{18}$	842	858	536	553

The IR spectra (MP2 Ext) are presented in Fig.3. The similarity of the vibrational bands is observed for  $\text{Na}_2\text{AlF}_5$  and  $\text{Na}_2\text{AlCl}_5$  for isomers of the same configurations. For example, in the spectra of the  $C_s$  isomers, the most intensive bands correspond to the Al-X asymmetrical stretching vibrations at  $891\text{ cm}^{-1}$  ( $\text{Na}_2\text{AlF}_5$ ) and

$588\text{ cm}^{-1}$  ( $\text{Na}_2\text{AlCl}_5$ ). The high intensities of bands assigned to Al-X modes are caused by the bigger number of Al-X bonds compared to Na-X; in both isomers Al atom links with four X atoms While Na atom, being the terminal, forms two or three bonds in  $C_{2v}$  and three in  $C_s$ .

**Table 4. Calculated properties of supersalts Na<sub>2</sub>AlX<sub>5</sub> (C<sub>s</sub> symmetry)**

Property	Na <sub>2</sub> AlF <sub>5</sub>		Na <sub>2</sub> AlCl <sub>5</sub>	
	B3P86 ext	MP2ext.	B3P86 ext	MP2ext.
-E	1066.73299	1065.22828	2868.50085	2865.22398
Re1 (Al-X)	1.656	1.655	2.104	2.092
Re2 (Al-X1)	1.707	1.702	2.179	2.162
Re3(Al-X2)	1.722	1.721	2.207	2.201
Re4 (Na-X1)	2.258	2.243	2.726	2.706
Re5(Na-X2)	2.483	2.417	2.893	2.828
Re6 (Na-X3)	2.053	2.034	2.525	2.528
ae <sub>1</sub> (X-Al-X1)	115.3	115.5	113.8	114.4
ae <sub>2</sub> (X-Al-X <sub>2</sub> )	116.9	116.3	113.5	112.8
ae <sub>3</sub> (Al-X1-Na)	99.9	98.5	90.6	88.9
ae <sub>4</sub> (X <sub>2</sub> -Na-X <sub>3</sub> )	85.6	85.6	93.1	93.6
ae <sub>5</sub> (Na-X3-Na)	102.4	102.3	88.2	88.2
ae <sub>6</sub> (X1-Na-X2)	66.4	67.7	75.3	78.2
-Δ <sub>r</sub> E <sub>iso</sub>	13.5	16.5	12.8	17.4
μ <sub>e</sub>	3.67	3.76	2.89	3.17
ω <sub>1</sub>	56	65	33	26
ω <sub>2</sub>	89	92	56	44
ω <sub>3</sub>	97	117	81	85
ω <sub>4</sub>	110	123	88	101
ω <sub>5</sub>	136	139	103	110
ω <sub>6</sub>	162	171	104	117
ω <sub>7</sub>	192	203	120	136
ω <sub>8</sub>	226	241	160	159
ω <sub>9</sub>	266	273	169	176
ω <sub>10</sub>	298	301	171	180
ω <sub>11</sub>	316	324	182	188
ω <sub>12</sub>	340	344	201	207
ω <sub>13</sub>	381	360	257	275
ω <sub>14</sub>	412	402	277	291
ω <sub>15</sub>	616	621	337	350
ω <sub>16</sub>	709	718	445	461
ω <sub>17</sub>	765	781	478	503
ω <sub>18</sub>	885	891	562	588

Note: Δ<sub>r</sub>E<sub>iso</sub> are the energies of the isomerization reactions Na<sub>2</sub>AlX<sub>5</sub> (C<sub>2v</sub>) = Na<sub>2</sub>AlX<sub>5</sub> (C<sub>s</sub>), in kJ mol<sup>-1</sup>

The valence vibrations of Al-X bonds are of higher frequency than those of Na-X; e.g. in the spectrum of Na<sub>2</sub>AlF<sub>5</sub>(C<sub>s</sub>), the bands at 891 and 781 cm<sup>-1</sup> are assigned to Al-F stretching modes whereas 717 and 402 correspond to Na-F stretching vibrations (Fig. 3b). The similar relationship is observed in spectrum of Na<sub>2</sub>AlCl<sub>5</sub> (C<sub>s</sub>), Fig. 3d. This relationship is accounted by the internuclear separations between metal and halide, i.e. shorter the distance higher is the frequency.

To evaluate the concentration of two isomers in the equilibrium vapour, the isomerization reactions



were considered. The isomerization energies Δ<sub>r</sub>E<sub>iso</sub> were calculated by equation.

$$\Delta_r E_{\text{iso}} = E(\text{C}_s) - E(\text{C}_{2v}) \quad (1)$$

and given in Table 4. The values of Δ<sub>r</sub>E<sub>iso</sub> are negative: -16.5 kJ mol<sup>-1</sup> (Na<sub>2</sub>AlF<sub>5</sub>) and -17.4 kJ mol<sup>-1</sup> (Na<sub>2</sub>AlCl<sub>5</sub>), according to MP2Ext calculations; therefore the C<sub>s</sub> isomer is more stable energetically as compared to C<sub>2v</sub> isomer for both species. Their relative abundance in saturated vapour was estimated using the following equation:

$$\Delta_r H^\circ(0) = T\Delta_r \Phi^\circ(T) - RT \ln \left( \frac{p_{II}}{p_I} \right), \quad (2)$$

Where Δ<sub>r</sub>H<sup>o</sup>(0) is the enthalpy of the reaction; T is absolute temperature; Δ<sub>r</sub>Φ<sup>o</sup>(T) is the change in the reduced Gibbs energy of the reaction, Φ<sup>o</sup>(T) = -[H<sup>o</sup>(T) - H<sup>o</sup>(0) - TS<sup>o</sup>(T)]/T; p<sub>II</sub>/p<sub>I</sub> is the pressure ratio between two isomers, isomer I corresponds

to  $C_{2v}$ , and II corresponds to  $C_s$ . The thermodynamic functions of the isomers are given in Appendix. The enthalpies of the isomerization reactions  $\Delta_r H^\circ(0)$  were calculated using isomerization energies  $\Delta_r E_{\text{iso}}$  and the ZPVE corrections  $\Delta_r \epsilon$ . The values of  $\Phi^\circ(T)$  were calculated using the optimized coordinates and vibrational frequencies obtained by MP2 method with extended basis set. The relative concentrations have been calculated by MP2Ext for the temperature range 900 – 2000 K and the plots are displayed in Fig. 4.

The results show that for the whole temperature range  $C_{2v}$  isomer prevails in vapor despite of its energy being a bit higher than that of  $C_s$ . For example, at 1200 K the value of  $p_{\text{II}}/p_{\text{I}}$  equals to  $\sim 0.40$  and  $\sim 0.36$  for  $\text{Na}_2\text{AlF}_5$  and  $\text{Na}_2\text{AlCl}_5$ , respectively. The relative abundances of the two isomers in vapor varies with the temperature. Thus, as the temperature raises the relative

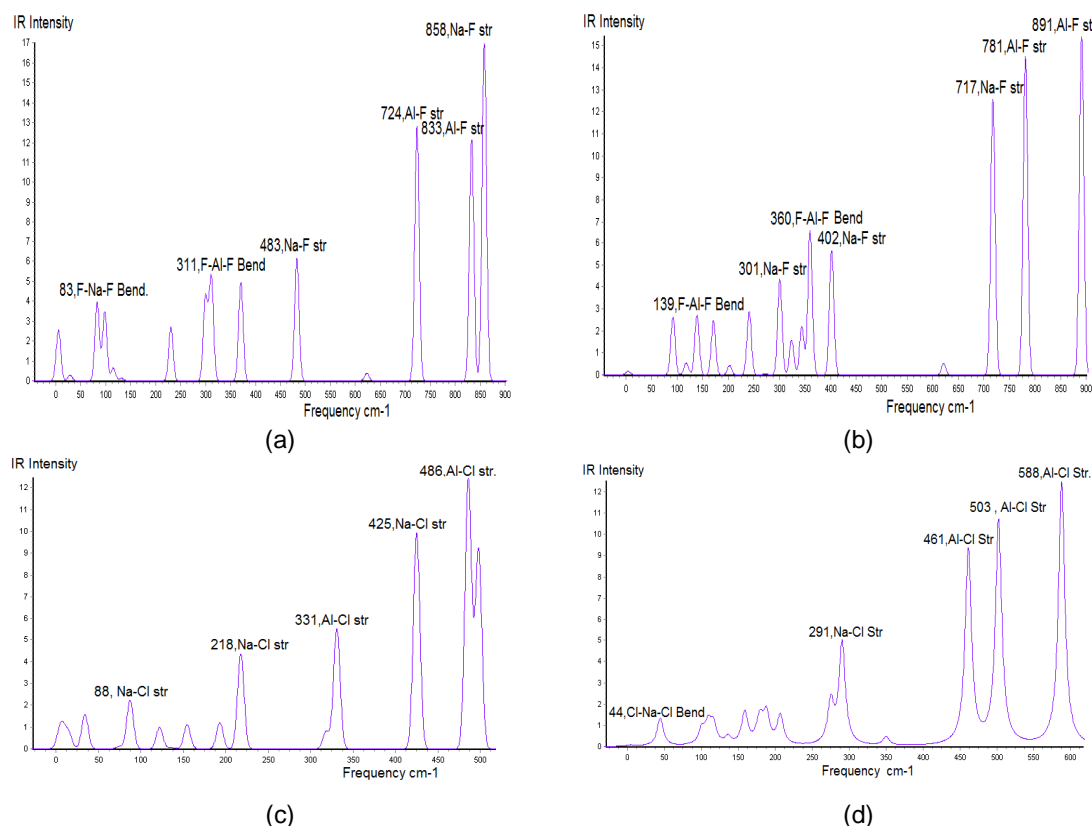
concentration of the  $C_s$  isomer decreases while that of the  $C_{2v}$  isomer becomes more abundant. For example, at 2000 K the value of  $p_{\text{II}}/p_{\text{I}}$  equals to  $\sim 0.20$  and  $\sim 0.18$  for  $\text{Na}_2\text{AlF}_5$  and  $\text{Na}_2\text{AlCl}_5$ , respectively.

### 3.4 Thermodynamic Properties of Supersalts

Different building blocks and routes have been considered to design the supersalts as presented by the following chemical reactions:



In reactions R2 and R3, the traditional salts,  $\text{AlX}_3$  and  $\text{NaX}$  or dimer  $\text{Na}_2\text{X}_2$ , are involved, while in R4 the ionic superhalogens



**Fig. 3. Theoretical infrared spectra (MP2 Ext) of supersalts: (a)  $\text{Na}_2\text{AlF}_5$  ( $C_{2v}$ ) (b)  $\text{Na}_2\text{AlF}_5$  ( $C_s$ ) (c)  $\text{Na}_2\text{AlCl}_5$  ( $C_{2v}$ ) (d)  $\text{Na}_2\text{AlCl}_5$  ( $C_s$ )**

$\text{AlX}_4^-$  and superalkalies  $\text{Na}_2\text{X}^+$  are used to form the supersalts.

The energies of reactions,  $\Delta_r E$ , zero-point vibration energy corrections,  $\Delta_r \varepsilon$ , enthalpies of the reactions,  $\Delta_r H^\circ(0)$  obtained by DFT and MP2 methods with extended basis set are presented in Table 5; these values correspond to the isomers of  $C_s$  symmetry of the supersalts as these isomers possess lower energies. For each reaction considered the difference between the  $\Delta_r H^\circ(0)$  values by B3P86 and MP2 methods appeared to be irregular in the range between  $\sim 15$  (for R3,  $\text{Na}_2\text{AlCl}_5$ ) and  $\sim 66$  (for R3,  $\text{Na}_2\text{AlF}_5$ )  $\text{kJ mol}^{-1}$ . All reactions were found to proceed by releasing energy (i.e., exothermic) as their calculated enthalpies of the reactions  $\Delta_r H^\circ(0)$  are negative. The energy released decreases in the rank  $\text{R2} \rightarrow \text{R4} \rightarrow \text{R3}$ ; the least energy corresponds to the channel R3 which involves the dimer  $\text{Na}_2\text{X}_2$ .

Using the same approach as in our previous study [7], we have estimated the enthalpies of formation  $\Delta_f H^\circ(0)$  of the supersalts. This was done through the enthalpies of all three types of reactions, given in Table 5. The enthalpies of formation of the building blocks are taken from literature:  $\text{NaX}$ ,  $\text{Na}_2\text{X}_2$ ,  $\text{AlX}_3$  [15],  $\text{Na}_2\text{F}^+$ [23],  $\text{Na}_2\text{Cl}^+$  [24],  $\text{AlF}_4^-$  [8], and  $\text{AlCl}_4^-$  [10].

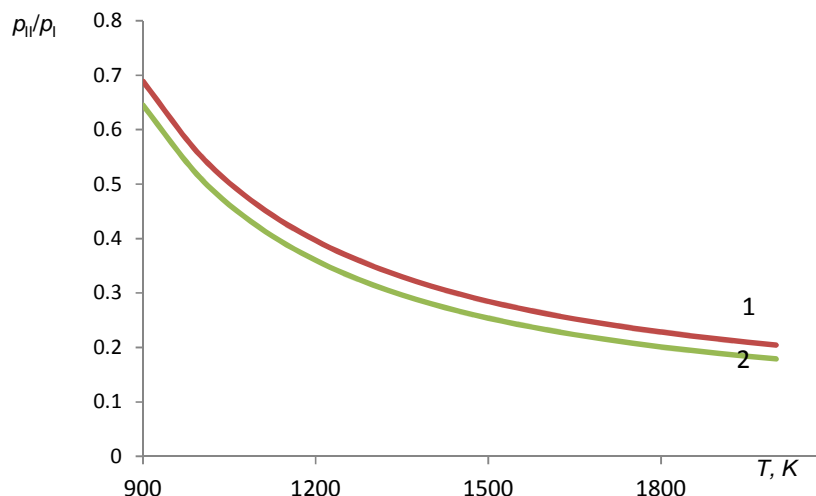
The computed  $\Delta_f H^\circ(0)$  results are presented in Table 5 and plotted in Fig. 5 vs. the theoretical

approach (regarding the type of the reaction and method DFT/B3P86 or MP2 applied). For two species,  $\text{Na}_2\text{AlF}_5$  and  $\text{Na}_2\text{AlCl}_5$ , a similar trend of oscillating  $\Delta_f H^\circ(0)$  values is observed along each plot. A fair agreement is seen between values of  $\Delta_f H^\circ(0)$  obtained by different methods for each supersalt. The averaged values of  $\Delta_f H^\circ(0)$  were accepted as enthalpies of formation of gas-phase supersalts:  $-2250 \pm 45 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\text{Na}_2\text{AlF}_5$ ) and  $-1380 \pm 20 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\text{Na}_2\text{AlCl}_5$ ) respectively. Evaluation of the accuracy of the results was done using data obtained by all three reactions through two approaches of calculations (B3P86 Ext, MP2 Ext) as a half difference between maximum and minimum values in the range.

The thermodynamic stability of the supersalts was examined through Gibbs free energy for the reaction R3 as it corresponds to the most probable channel of dissociation. The change in Gibbs free energy  $\Delta_r G^\circ(T)$  was calculated by the formula:

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T\Delta_r S^\circ(T) \quad (3)$$

Where  $\Delta_r H^\circ(T)$  is the enthalpy of the reaction,  $T$  is the absolute temperature;  $\Delta_r S^\circ$  is the entropy change. The required thermodynamic functions have been computed using rigid rotator-harmonic oscillator approximation, based on geometrical parameters and vibrational frequencies obtained in B3P86 method with the extended basis set.

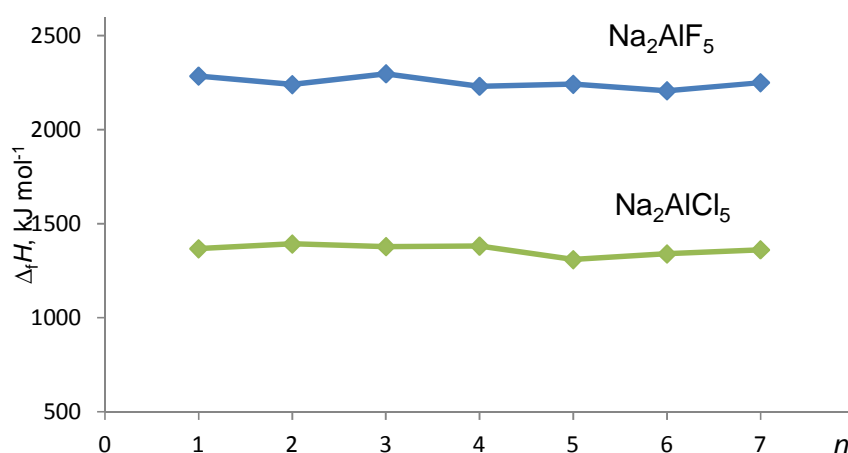


**Fig. 4.** Relative abundance  $p_1/p_2$  of two isomers of supersalts: 1-  $\text{Na}_2\text{AlF}_5$  and 2- $\text{Na}_2\text{AlCl}_5$ ; I is  $C_{2v}$  and II is  $C_s$  isomer (MP2Ext)

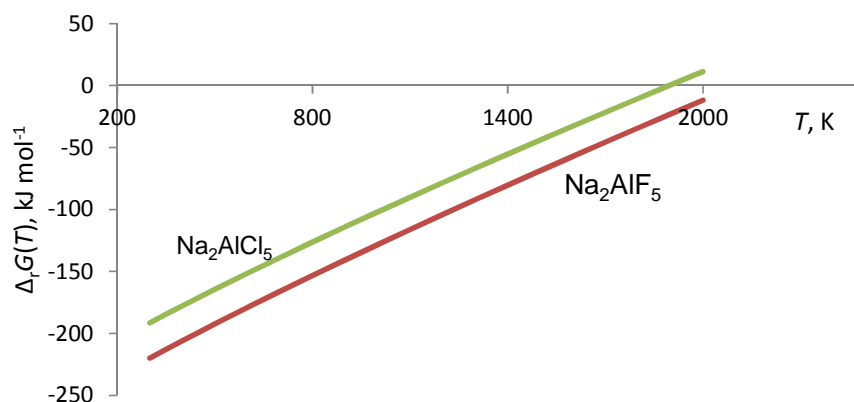


**Table 5.** The energies of reactions,  $\Delta_r E$ , zero-point vibration energy corrections,  $\Delta_r \epsilon$ , enthalpies of the reactions,  $\Delta_r H^{\circ}(0)$ , and enthalpies of formation,  $\Delta_f H^{\circ}(0)$  of supersalts  $\text{Na}_2\text{AlX}_5$  ( $\text{X} = \text{F}, \text{Cl}$ ); all values are given in  $\text{kJ} \cdot \text{mol}^{-1}$

Property	$-\Delta_r E$	$\Delta_r \epsilon$	$\text{Na}_2\text{AlF}_5$		$\text{Na}_2\text{AlCl}_5$		$-\Delta_r H^{\circ}(0)$	$-\Delta_f H^{\circ}(0)$
			$-\Delta_r H^{\circ}(0)$	$-\Delta_f H^{\circ}(0)$	$-\Delta_r H^{\circ}(0)$	$-\Delta_f H^{\circ}(0)$		
<b>R2</b>								
B3P86 Ext	503.6	10.7	492.9	2285	429.8	5.2	424.6	1368
MP2 Ext	459.4	11.4	447.9	2240	456.6	6.9	449.7	1393
<b>R3</b>								
B3P86 Ext	266.0	2.9	263.1	2298	255.8	2.1	253.7	1379
MP2 Ext	200.2	3.4	196.8	2231	242.0	3.9	238.1	1382
<b>R4</b>								
B3P86 Ext	368.2	2.6	365.6	2242	416.8	3.0	413.8	1310
MP2 Ext	333.1	2.8	330.3	2207	448.1	4.5	443.6	1340



**Fig. 5.** The enthalpies of formation of the supersalts calculated through different approaches:  $n = 1, 2$  correspond to reaction  $2\text{NaX} + \text{AlX}_3 = \text{Na}_2\text{AlX}_5$  (1- B3P86 EXT, 2- MP2 EXT);  $n = 3, 4$  correspond to reaction  $\text{Na}_2\text{X}_2 + \text{AlX}_3 = \text{Na}_2\text{AlX}_5$  (3- B3P86 EXT, 4- MP2 EXT);  $n=5,6$  correspond to reaction  $\text{Na}_2\text{X}^+ + \text{AlX}_4^- = \text{Na}_2\text{AlX}_5$  (5- B3P86 EXT, 6- MP2 EXT);  $n=7$  correspond to the averaged values



**Fig. 6.** Gibbs free energy change against temperature for reaction  $\text{Na}_2\text{X}_2 + \text{AlX}_3 = \text{Na}_2\text{AlX}_5$ ; the isomer of Cs symmetry for  $\text{Na}_2\text{AlX}_5$  was considered

The thermodynamic functions for the supersalts used in this study are listed in Tables A and B of the Appendix. In the  $\Delta_r G^\circ(T)$  calculations, the isomer of  $C_s$  symmetry for  $Na_2AlX_5$  was considered. The graph of  $\Delta_r G^\circ(T)$  vs  $T$  is shown on the Fig. 6. As it is seen the values are negative in a broad temperature range implying that the reaction for the supersalt formation is feasible.

The spontaneous dissociation of the supersalts starts at the elevated temperatures, at about  $\sim 2100$  K for  $Na_2AlF_5$  and  $\sim 1900$  K for  $Na_2AlCl_5$ . These temperatures for  $Na_2AlX_5$  are higher than for  $Na_2MgX_4$  supersalts studied in [7]. The calculated  $\Delta_r G^\circ$  values indicate the thermodynamic stability of the supersalts. The lower thermodynamic stability of  $Na_2AlCl_5$  as compared to  $Na_2AlF_5$  is accounted for stronger chemical bonds in the latter. The spontaneous course for other reactions R3 and R4 is predictable as the enthalpies of these reactions are more negative than for R2.

#### 4. CONCLUSION

In this work we have theoretically predicted the formation of supersalts  $Na_2AlX_5$  ( $X = F, Cl$ ) through interaction between different building blocks. DFT/B3P86 and MP2 methods have been used to determine the geometrical parameters and vibrational frequencies of the building blocks: superalkalies  $Na_2X$ , superhalogens  $AlX_4^-$ , dimers  $Na_2X_2$  and supersalts  $Na_2AlX_5$  ( $X = F, Cl$ ). It is found that DFT and MP2 results are in good agreement with each other and with the available reference data. The predictable stability and existence of the supersalts  $Na_2AlF_5$  and  $Na_2AlCl_5$  is supposed to relate to low ionization energies and high electron affinities of the superalkalies and superhalogens respectively.

Two isomeric forms, compact structure of  $C_s$  symmetry and two-cycled structure of  $C_{2v}$  symmetry, were found to exist for both supersalts. Evaluation of the relative concentrations of the isomers in equilibrium vapour was done and found that  $C_{2v}$  isomer prevails at elevated temperatures. The computed values of enthalpies and Gibbs energies of association reactions indicated high thermodynamic stability of the supersalts and spontaneity of the salt formation process in a broad temperature range.

All these findings have a potential impact on the design and synthesis of novel inorganic

materials. For instance the designed supersalts are predicted to be useful in catalysis, ion batteries manufacturing, quantitative and qualitative analysis, chemical synthesis, making food preservatives and condiments, etc. Along similar lines the designed superhalogens can be protonated to form novel acids as they have higher electronegativity values than their respective normal halogen atoms. So we hope that this study will stimulate experimental and technological efforts in the synthesis of salts and its derivatives through interaction of different building blocks.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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## APPENDIX

Table A and B present the molar heat capacity  $c_p(T)$ ; Gibbs reduced free energy  $\Phi(T)$ ; entropy  $S(T)$ ; and enthalpy increment  $H(T) - H(0)$ , as the thermodynamic functions of supersalts  $\text{Na}_2\text{AlF}_5$  and  $\text{Na}_2\text{AlCl}_5$  in gaseous phase which were calculated using Openthermo software [11], and are in  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively, are listed in Table A and B. The geometrical parameter and vibrational frequencies were calculated by B3P86 method with extended basis set.

Table A. Thermodynamic functions of  $\text{Na}_2\text{AlF}_5$ 

T, K	$c_p(T)$	$\Phi(T)$	$S(T)$	$H(T) - H(0)$	T, K	$c_p(T)$	$\Phi(T)$	$S(T)$	$H(T) - H(0)$
<b><math>C_{2v}</math> isomer</b>					<b><math>C_s</math> isomer</b>				
298.15	151.28	356.26	466.949	33.003	298.15	150.12	330.947	435.643	31.215
500	168.34	418.84	549.952	65.556	500	167.96	391.017	518.285	63.634
600	172.26	443.35	581.017	82.601	600	172	414.881	549.292	80.647
700	174.83	464.97	607.778	99.964	700	174.64	436.035	576.017	97.987
800	176.59	484.32	631.245	117.54	800	176.45	455.028	599.462	115.547
900	177.84	501.83	652.121	135.266	900	177.72	472.256	620.322	133.259
1000	178.77	517.81	670.908	153.098	1000	178.67	488.018	639.099	151.081
1100	179.45	532.52	687.980	171.010	1100	179.38	502.540	656.163	168.985
1200	179.99	546.13	703.619	188.984	1200	179.93	516.003	671.795	186.951
1300	180.41	558.81	718.043	207.005	1300	180.35	528.548	686.214	204.966
1400	180.75	570.67	731.425	225.063	1400	180.71	540.294	699.593	223.019
1500	181.03	581.80	743.905	243.152	1500	180.97	551.335	712.070	241.103
1600	181.27	592.30	755.596	261.266	1600	181.22	561.750	723.758	259.213
1700	181.45	602.24	766.589	279.4	1700	181.41	571.606	734.75	277.344
1800	181.56	611.66	776.965	297.552	1800	181.54	580.960	745.123	295.493
1900	181.72	620.62	786.786	315.718	1900	181.67	589.861	754.943	313.656
2000	181.85	629.16	796.111	333.897	2000	181.82	598.350	764.266	331.832

Table B. Thermodynamic functions of  $\text{Na}_2\text{AlCl}_5$ 

T, K	$c_p(T)$	$\Phi(T)$	$S(T)$	$H(T) - H(0)$	T, K	$c_p(T)$	$\Phi(T)$	$S(T)$	$H(T) - H(0)$
<b><math>C_{2v}</math> isomer</b>					<b><math>C_s</math> isomer</b>				
298.15	166.67	406.348	534.255	38.136	298.15	166.67	409.745	534.255	37.123
500	176.38	477.326	623.262	72.968	500	176.46	450.079	594.028	71.974
600	178.28	504.420	655.602	90.709	600	178.33	476.844	626.381	89.722
700	179.46	528.036	683.179	108.600	700	179.51	500.225	653.966	107.619
800	180.25	548.962	707.197	126.588	800	180.29	520.976	677.99	125.611
900	180.79	567.748	728.461	144.642	900	180.82	539.626	699.257	143.668
1000	181.19	584.789	747.531	162.742	1000	181.22	556.559	718.330	161.771
1100	181.48	600.382	764.815	180.876	1100	181.51	572.064	735.616	179.907
1200	181.71	614.752	780.616	199.037	1200	181.74	586.362	751.419	198.069
1300	181.9	628.078	795.168	217.217	1300	181.9	599.625	765.972	216.251
1400	182.04	640.500	808.652	235.413	1400	182.04	611.994	779.458	234.449
1500	182.15	652.134	821.215	253.622	1500	182.13	623.583	792.022	252.659
1600	182.24	663.072	832.973	271.841	1600	182.24	634.482	803.781	270.879
1700	182.34	673.396	844.024	290.068	1700	182.33	644.769	814.832	289.107
1800	182.36	683.167	854.446	308.303	1800	182.38	654.509	825.255	307.343
1900	182.41	692.443	864.308	326.543	1900	182.4	663.757	835.117	325.584
2000	182.52	701.273	873.667	344.789	2000	182.51	672.561	844.476	343.831

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