

Cluster Ions in Vapour over Calcium Dichloride: Theoretical Study of Geometrical Structure and Vibrational Spectra

Ibrahim Moustapher^{1*}, Tatiana P. Pogrebnaya¹ and Alexander M. Pogrebnoi¹

¹Department of Materials, Energy Science and Engineering, The Nelson Mandela African Institution of Science and Technology (NM-AIST), Arusha, Tanzania.

Authors' contributions

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

Article Information

DOI: 10.9734/BJAST/2016/21810

Editor(s):

(1) Rui Xiao, School of Energy and Environment, Southeast University, China.

Reviewers:

(1) Yongchun Zhu, Shenyang Normal University, China.

(2) Angélica Machi Lazarin, Universidade Estadual de Maringá, Maringá, Brazil.

Complete Peer review History: <http://sciencedomain.org/review-history/11665>

Original Research Article

Received 4th September 2015
Accepted 19th September 2015
Published 5th October 2015

ABSTRACT

Geometrical structure and vibrational spectra for CaCl_3^- , Ca_2Cl_3^+ , Ca_3Cl_5^+ , Ca_4Cl_7^+ , and Ca_5Cl_9^+ ions have been studied by employing density functional theory and the second order Møller–Plesset perturbation theory. The equilibrium geometrical structures are as follows: the planar D_{3h} for CaCl_3^- , triple-bridged bipyramid D_{3h} for Ca_2Cl_3^+ , hexa-bridged bipyramid D_{3h} for Ca_3Cl_5^+ , polyhedral C_{2v} for Ca_4Cl_7^+ , and polyhedral D_{3h} for Ca_5Cl_9^+ . No isomers have been confirmed to exist.

Keywords: Calcium chloride; cluster ions; DFT; MP2; geometrical parameters; fundamental frequencies.

*Corresponding author: E-mail: moustapheri@nm-aist.ac.tz;

1. INTRODUCTION

Cluster ions have a potential interest for scientists and researchers owing to the possibilities of designing and fabricating new materials. Due to their size and composition, some cluster ions have unique electronic, optical and magnetic properties [1–3]. These species can serve as fundamental building blocks for a new class of materials with desired properties [3, 4]. Generally, the cluster ions may be considered as structural elements forming a bridge between the gaseous phase and crystal matter.

Different compounds containing calcium and chlorine have been proved to have many applications ranging from the society to industries [5,6]. Numerous studies on cluster ions have been done by the combination of mass spectrometry and different ionization techniques; such as electron ionization, chemical ionization, field ionization, and others [7–9]. Mass spectrometry is a powerful instrumental technique which is used for investigation of inorganic and organic compounds [7]. It is capable of a broad analysis and characterization of molecular and ionic species [10]. For the treatment of the experimental data, the thermodynamic functions of the ions and molecules are required. To calculate the thermodynamic functions, the geometrical parameters and vibrational frequencies are needed, however they are difficult to be measured by available experimental techniques [11]. Quantum mechanical methods now provide reliable data on the structure and properties of the ions.

The geometrical parameters and vibrational spectra of alkaline earth dihalides MX_2 , and monohalides MX ($M = Mg, Ca, Sr, Ba$; $X = F, Cl, Br, I$) have been the subject of many experimental [12–16] and theoretical works [17–20]. Extensive investigations on alkali earth halide superhalogens, MX_3^- ($M = Be, Mg, Ca$; $X = F, Cl, Br$), as well as species with mixed halide ligands have been performed earlier [21–23]. It has been observed experimentally by mass spectrometric technique that calcium chloride gives ions of the type $[(CaCl_2)_n + CaCl]^+$ and $[(CaCl_2)_n + Cl]^-$ in vapour phase [7]. The ion-molecular equilibria involving $CaCl^+$, $Ca_2Cl_3^+$, $Ca_3Cl_5^+$, and $Ca_4Cl_7^+$ positive ions were detected and investigated in [24]. Spectroscopic data for molecular and cluster ions are unavailable or scarce. Recently, the barium chloride cluster ions $Ba_2Cl_3^+$, $Ba_3Cl_5^+$, $Ba_4Cl_7^+$ and $BaCl_3^-$ have been studied by quantum chemical methods [25].

The aim of the present quantum chemical study is to determine the equilibrium geometrical configuration, geometrical parameters, and normal vibration frequencies of the $CaCl_3^-$, $Ca_2Cl_3^+$, $Ca_3Cl_5^+$, $Ca_4Cl_7^+$, and $Ca_5Cl_9^+$ and reveal possible isomers among the alternative structures of the ions.

2. COMPUTATIONAL DETAILS

The calculations were performed employing the GAMESS (General Atomic and Molecular Electronic Structure System) program [26], Firefly version 8.1.0 [27]. Density functional theory (DFT) with the non-local correlation Becke–Perdew 86 (B3P86) functional [28–30] and the second order Møller–Plesset perturbation theory (MP2) were implemented in optimization of geometrical parameters and calculation of vibrational frequencies. Two basis sets were applied: B1 and B2. The basis B1 was the McLean–Chandler basis set 8s4p1d for Ca and 6s5p1d for Cl, incorporated in [26]. More extended basis B2 was the valence correlation consistent cc-pVTZ 6s5p3d1f basis set for Ca and aug-cc-pVTZ 6s5p3d2f for Cl taken from the basis set library EMSL [31–33]. The combination of the two methods (DFT and MP2) and two basis sets (B1 and B2) provided the following four theoretical approximations: DFT B1, MP2 B1, DFT B2, and MP2 B2.

All four theoretical methods were used in computation of properties of the diatomic species $CaCl$, $CaCl^+$, and monomer molecule $CaCl_2$ to analyze how the basis set and the computational method applied affect the results. The properties of the ions $CaCl_3^-$, $Ca_2Cl_3^+$, and $Ca_3Cl_5^+$ were computed by all four methods, the results obtained by DFT B2 and MP2 B2 are presented in this work. The DFT B1 and MP2 B1 were applied in computation of properties of the $Ca_4Cl_7^+$ and only DFT B1 for the heaviest $Ca_5Cl_9^+$ ion due to limited computer resources. For visualization of shapes, parameters and vibrational spectra, wxMacMolPlt [34] and Chem Craft [35] software were used.

3. RESULTS AND DISCUSSION

3.1 Calcium Monochloride Molecule $CaCl$, Diatomic Ion $CaCl^+$, and Calcium Dichloride Molecule $CaCl_2$

Four theoretical approaches DFT B1, MP2 B1, DFT B2 and MP2 B2 were used to compute the geometrical parameters and vibrational frequencies of the diatomic species $CaCl$, $CaCl^+$,

and monomer molecule CaCl_2 . To check applicability of the methods used, the calculated equilibrium geometrical parameters and other properties of these species were compared with the available reference data obtained experimentally [12-14,16,36-45] and theoretically using more advanced CCSD(T) method [17]. The results are presented in Table 1.

The graph for equilibrium internuclear distances $R_e(\text{Ca}-\text{Cl})$ in CaCl , CaCl^+ , and CaCl_2 species against the method of determination is shown in Fig. 1. The plot for BaCl from [25] is included for comparison. The trend observed for the CaCl species is alike to that for BaCl that is decreasing of R_e values along the plot when proceed from DFT B1 \rightarrow MP2 B2; but for BaCl the plot is smooth while for CaCl species the plots are zigzag shaped. For all species, the internuclear distances obtained with B2, both DFT and MP2, agree well with the experimental and theoretical reference data available; while the results by the B1 are essentially overrated, particularly it is observed for the diatomic ion CaCl^+ for which the $R_e(\text{Ca}-\text{Cl})$ computed with B1 is overrated by 0.12

Å compared to that found with B2. The magnitudes of the dipole moment for CaCl and CaCl^+ correlate with the equilibrium internuclear distance for the pairs of the data found by DFT B1– DFT B2 or by MP2 B1– MP2 B2: The smaller the distance, the smaller the dipole moment magnitude.

The molecule CaCl_2 was confirmed to be linear, $D_{\infty h}$, in agreement with literature data [12–14b and 41]. It is worth to mention how the structure changes in series of alkali-earth metal dihalides MX_2 molecules ($M = \text{Ca}, \text{Sr}, \text{Ba}; X = \text{F}, \text{Cl}, \text{Br}$). Different experimental techniques, such as electric beam deflection and gas-phase electron diffraction study by Klemperer et al. [15] and vibrational spectroscopic studies [14] have been applied to state the shape of MX_2 molecules. Also quantum chemical calculations have been carried out [12,20] and confirmed that the structure of alkali-earth metal dihalides was bent for CaF_2 , SrF_2 , SrCl_2 and barium dihalides but linear for others. The various reasons why some MX_2 are bent while others are linear were analyzed and discussed [19,20].

Table 1. Theoretical and experimental parameters of the CaCl , CaCl^+ , and CaCl_2 species

Property ^a	DFT B1	MP2 B1	DFT B2	MP2 B2	Reference
CaCl					
$R_e(\text{Ca}-\text{Cl})$	2.563	2.563	2.426	2.426	2.437 [36], 2.439 [37]
$-E$	1137.79212	1136.58079	1137.86201	1136.80828	
ω_e	331		373		367.53 [37], 368 [38]
μ_e	8.53		4.05		
EA	1.29		1.23		
IE_{ad}	6.22		6.01		5.86±0.07 [39,38]
IE_{vert}	6.27	5.68	6.08	5.97	6.01±0.10 [40,38]
CaCl⁺					
$R_e(\text{Ca}-\text{Cl})$	2.465	2.470	2.314	2.350	
$-E$	1137.56365	1136.37216	1137.64120	1136.58889	
ω_e	409 (1.51)	414 (1.86)	454 (2.53)	441 (2.70)	
$-E$	1137.56365	1136.37216	1137.64120	1136.58889	
μ_e	8.1	9.3	5.4	6.8	
CaCl₂					
$R_e(\text{Ca}-\text{Cl})$	2.526	2.531	2.460	2.482	2.483 [12], 2.483 [13], 2.455 [14b]
$\alpha_e(\text{Cl}-\text{Ca}-\text{Cl})$	180	180	180	180	180 [12–14b, 41]
$-E$	1598.10447	1596.38062	1598.18823	1596.68708	
$\omega_1 (\Sigma_g^+)$	273	279	282	276	243 [14], 238 [16]
$\omega_2 (\Pi_u)$	61	68	27	37	69 [12], 64 [14], 66 [42], 72 [42]
$\omega_3 (\Sigma_u^+)$	439	446	423	422	402 [14], 403 [42], 414 [43], 395 [16], 397 [42], 394 [43]
IE_{ad}	9.74		9.65		
IE_{vert}	11.6	9.58	10.53	11.11	10.5±0.3 [44,38], 10.2 [45,38]

^a Here and hereafter in Tables 2–7 $R_e(\text{Ca}-\text{Cl})$ is the equilibrium internuclear distance, Å; valence angle $\alpha_e(\text{Cl}-\text{Ca}-\text{Cl})$, degrees; ω_e is the normal mode frequency, cm^{-1} ; μ_e is the dipole moment, D; IE is the ionization energy, eV

The calculated vibrational frequencies for CaCl and CaCl₂ molecules are compared to literature data obtained experimentally (infrared spectra in gas phase [12,14,16,37,38,42,43] and in solid matrices [14], and theoretically by CCSD (T) [17]. For the diatomic CaCl molecule, the vibrational frequency computed by DFT B2 is close to the experimental results [37,38] (Table 1) and theoretical value 368 cm⁻¹ [17]. For the diatomic species, CaCl, CaCl⁺, and BaCl⁺, the plot of frequencies ω_e versus method is given in Fig. 2. This plot correlates in general with that for the internuclear separations in Fig. 1, namely the values of R_e decrease from left to right and ω_e increase.

do not contradict to the experimental values, being overrated, by ~5–12%. For the deformational frequency ω_2 , there is a great difference between the B1 and B2 values; the results obtained with basis set B1 are in an acceptable agreement with the experimental values. Worth to note that the vibrational frequencies ω_1 , ω_2 , and ω_3 calculated by MP2 B2 method are very close to the theoretical result, $\omega_1 = 277$ cm⁻¹, $\omega_2 = 38$ cm⁻¹, $\omega_3 = 421$ cm⁻¹, obtained by CCSD(T) [17]. As concerns the deformational frequency ω_2 , the contradiction between the theoretical high level computation and experimental results had been discussed already earlier [12]. The problem is common for other alkali-earth dihalides and the contradiction may relate to the shallow bending potential of these molecules as well as matrix effect [12].

In the vibrational spectrum of CaCl₂ molecule (Table 1) the valence frequencies calculated by four methods agree well between each other and

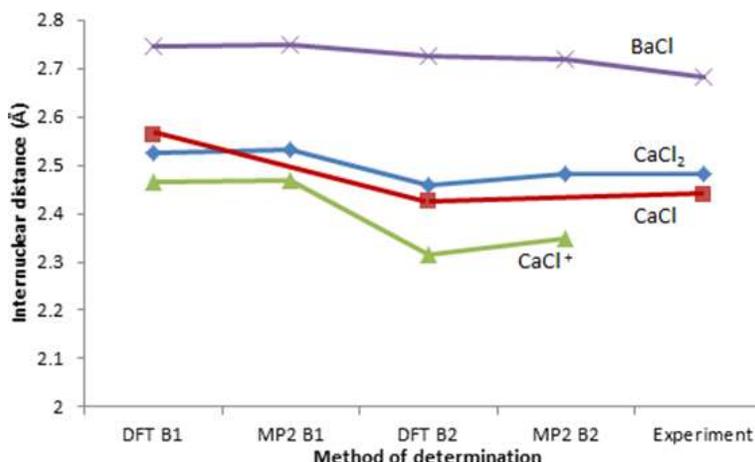


Fig. 1. Internuclear distance R_e (Å) in the CaCl, CaCl⁺, BaCl [25], and CaCl₂ versus method of determination

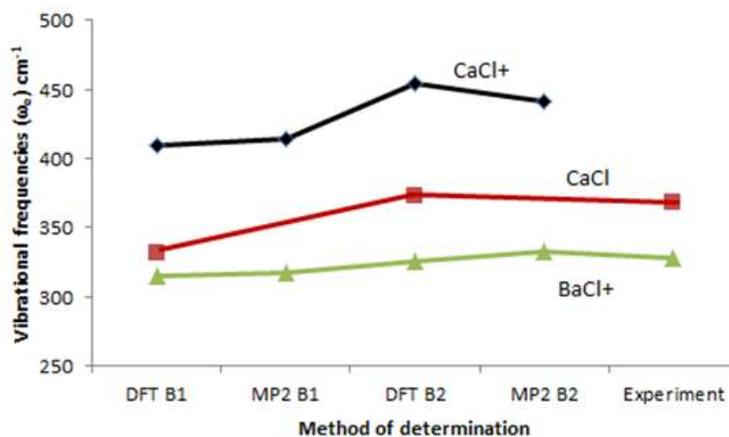


Fig. 2. Frequency of vibration ω_e (cm⁻¹) in the CaCl, CaCl⁺, and BaCl⁺ [25] versus method of determination

The ionization energies of neutral molecules have been computed; the vertical and adiabatic. Adiabatic ionization energy (IE_{ad}) was obtained as the difference between the total energies of neutral and ionized particles with the geometry optimized for each species. The values of IE_{ad} for CaCl calculated with DFT B2 are in good agreement with experimental data [38,39]. Vertical ionization energy (IE_{vert}) is defined as the difference between energies of the vibrational ground state of the neutral species and that of the positive ion [46]. The optimized geometry was calculated for neutral species, CaCl and CaCl₂, and accepted the same for positive ions, CaCl⁺ and CaCl₂⁺. The values of IE_{vert} computed by DFT B2 and MP2 B2 for CaCl and CaCl₂ molecules are in the acceptable range when compared with the experimental values [38,40] and [38,44,45], respectively.

Concluding this comparison of the calculated and available experimental data, we can state that DFT and MP2 methods with basis B2 provide the properties of the suitable accuracy and we expect the similar quality of the results for the heavier species.

3.2 Tetraatomic Negative Ion CaCl₃⁻ and Neutral Species CaCl₃

The geometrical structure of the CaCl₃⁻ ion was found to be planar of D_{3h} symmetry. For the neutral CaCl₃ species two configurations were considered, C_{2v} and D_{3h} . Among them the former was confirmed to be equilibrium while for the latter, the imaginary frequencies have been revealed and the total energy was higher by 45.7 kJ·mol⁻¹ (DFT) and 130 kJ·mol⁻¹ (MP2) compared to C_{2v} structure. The electronic state of the CaCl₃⁻ ion is ¹A₁' and that of the neutral CaCl₃ is ²B₂. The equilibrium geometrical configurations of the CaCl₃⁻ ion and CaCl₃ neutral species are shown in Fig. 3 and the properties are reported in Table 2. It is seen that the geometrical parameters and vibrational spectra calculated by DFT B2 and MP2 B2 do not contradict each other and the theoretical results [22] obtained through CCSD(T)/6-311+G method.

Vertical detachment energy (VED) has been calculated as the difference between energies of the neutral and ionic species, the structure of the ion being optimized and accepted the same (D_{3h}) for the neutral. As is seen the magnitude of VED by MP2 B2 agrees better (than that by DFT B2) with the experimental result [22], being still

overrated by ~0.3 eV. Adiabatic electron affinity of the CaCl₃ neutral particle is in good accordance between both methods and theoretical value [22].

3.3 Pentaatomic Positive Ion Ca₂Cl₃⁺

Several shapes, such as linear, kite-shaped, and bipyramidal have been considered. The first two structures were found to be nonequilibrium due to the appearance of imaginary frequencies. Only the bipyramidal configuration of the D_{3h} symmetry was confirmed to be the equilibrium structure for the Ca₂Cl₃⁺, in which the calcium atoms were in the vertices of the bipyramid and the chlorine atoms in the horizontal plane (Fig. 4). The parameters obtained by DFT B2 and MP2 B2 method for the Ca₂Cl₃⁺ ion of D_{3h} symmetry are given in Table 3.

The geometrical parameters and vibration frequencies obtained by the DFT and MP2 methods are close to each other, respectively. Note, that the vibrational spectrum of the Ca₂Cl₃⁺ ion does not contain low frequencies. Thus the structure of this ion is compact and rigid. The most intensive bands are ω_3 (A_2'') = 284 cm⁻¹ and ω_4 (E') = 304 cm⁻¹ (MP2 B2), which correspond to antisymmetrical stretching Ca-Cl vibrations; the mode ω_5 (E') = 122 cm⁻¹ is bending Cl-Ca-Cl vibration.

If compare the parameters of the Ca₂Cl₃⁺ ion with those of the similar Ba₂Cl₃⁺ ion studied previously [25], then for the latter the bipyramidal configuration (D_{3h}) was found to be equilibrium as well and no other isomers were revealed.

It is also worth to compare the bipyramidal configuration of the Ca₂Cl₃⁺ ion to that of the neutral dimer molecule Ca₂Cl₄. The same theoretical approaches, DFT B2 and MP2 B2, were applied to compute the molecular parameters of the dimeric molecule Ca₂Cl₄. Two isomeric configurations were proved to exist: the planar cyclic configuration of D_{2h} symmetry, and bipyramid with a Cl-atom-tail of C_{3v} symmetry (Figs. 5a and 5b). The calculated molecular parameters are displayed in Table 4. The ion Ca₂Cl₃⁺, compared to dimer molecule Ca₂Cl₄ of C_{3v} symmetry, looks more compact and stable, as far as detachment of the terminal loose Cl atom from the neutral dimer favours the stabilization of the ion. For the planar shape of Ca₂Cl₄ molecule, low deformational frequencies are found, ω_8 = 20 cm⁻¹ (DFT B2) and 24 cm⁻¹ (MP2 B2), ω_{10} = 40 cm⁻¹ (DFT B2) and 41 cm⁻¹ (MP2 B2) which correspond to the bending mode

of the terminal Ca-Cl bonds. In the bipyramidal configuration (C_{3v}) the lowest frequency, $\omega_8 = 50 \text{ cm}^{-1}$ (DFT B2 and MP2 B2), corresponds to the bending of the Cl-tail fragment. Thus the bipyramidal structure looks as compact and more rigid compared to the planar one. It has lower energy than planar configuration, by $4 \text{ kJ}\cdot\text{mol}^{-1}$ (DFT B2) and $22 \text{ kJ}\cdot\text{mol}^{-1}$ (MP2 B2). Worth to mention that when computed with the McLean–Chandler basis set, the opposite result has been obtained that is the bipyramidal structure corresponds to higher energy, by $10 \text{ kJ}\cdot\text{mol}^{-1}$ (DFT B1) and $13 \text{ kJ}\cdot\text{mol}^{-1}$ (MP2 B1), than the planar one. According to the theoretical study [12b, 12c], the structure of D_{2h} symmetry was more stable by $2.5 \text{ kJ}\cdot\text{mol}^{-1}$, and that of C_{3v} was found to be nonequilibrium due to imaginary frequencies. We do not consider these results to

be dramatically controversial but they show that these two structures are comparable by energy and isomers may coexist in equilibrium vapour.

3.4 Octaatomic Positive Ion Ca_3Cl_5^+

Two possible configurations of the ions were considered; bipyramidal of D_{3h} symmetry and C_{2v} symmetry, in the latter two Ca_2Cl_2 cyclic fragments are located in the mutually perpendicular planes (Fig. 6). The two-cycled configuration was found of higher energy, by $193 \text{ kJ}\cdot\text{mol}^{-1}$ compared to bipyramidal, and several very low frequencies relating to the bending modes were revealed in the range between 7 and 40 cm^{-1} . This structure is not considered further and only the bipyramidal one has been examined.

Table 2. Properties of the tetraatomic species: CaCl_3^- ion (D_{3h} , A_1') and CaCl_3 neutral (C_{2v} , B_2)

Property ^a	DFT B2	MP2 B2	Reference [22] ^b
CaCl_3^- (D_{3h}, A_1')			
$R_e(\text{Ca-Cl})$	2.547	2.562	2.566
$-E$	2058.57510	2056.62576	2056.30100
VDE	5.81	6.93	6.62 ^c
ω_1 (A_1')	239	213	242
ω_2 (A_2'')	93 (1.31)	96 (1.41)	100
ω_3 (E')	330 (6.83)	341 (6.42)	344
ω_4 (E')	76 (0.26)	76 (0.36)	80
CaCl_3 (C_{2v}, B_2)			
$R_e(\text{Ca-Cl}_1)$	2.448	2.448	2.473
$R_e(\text{Ca-Cl})$	2.623	2.623	2.639
$\alpha_e(\text{Cl-Ca-Cl})$	61.3	61.3	62.1
$-E$	2058.37900	2056.42069	2056.10365
EA_{ad}	5.34	5.58	5.37
ω_1 (A_1)	403 (4.82)		412
ω_2 (A_1)	262 (0.01)		260
ω_3 (A_1)	184 (0.12)		181
ω_4 (B_1)	43 (1.11)		38
ω_5 (B_2)	227 (0.16)		216
ω_6 (B_2)	49 (0.57)		49

^a Here and hereafter, the values given in parentheses near the frequencies are infrared intensities in $D^2 \text{ amu}^{-1} \text{ \AA}^{-2}$. For the vibrational modes which are not active in IR spectra due to symmetry the zero values intensities are not indicated. The irreducible vibrational representations are $\Gamma = A_1' + A_2'' + 2E'$ for CaCl_3^- and $\Gamma = 3A_1 + B_1 + 2B_2$ for CaCl_3 . ^b Theoretical values from [22] calculated using CCSD(T)/6-311+G method.

^c Experimental value determined by photoelectron spectroscopy [22]



Fig. 3. The geometrical structure for (a) CaCl_3^- of D_{3h} symmetry; (b) CaCl_3 of C_{2v} symmetry

The parameters of the ion Ca_3Cl_5^+ (D_{3h}) are reported in Table 5. There are two kinds of equilibrium internuclear distances Ca–Cl: $R_e(\text{Ca}-\text{Cl}_v)$ and $R_e(\text{Ca}-\text{Cl}_h)$ where Cl_v and Cl_h denote the chlorine atoms in the vertex and horizontal plane of the bipyramid, respectively. The basis of the bipyramid is hexagon formed by three Ca and three Cl atoms. The internuclear separation between two Cl_h atoms (5.182 Å, MP2 B2) is much larger than that between two Cl_v , (3.558 Å, MP2 B2), the Ca– Cl_h bond being shorter than Ca– Cl_v one, by 0.07–0.08 Å. The bond angle at the vertex of bipyramid is acute, 82° , close to that in the Ca_2Cl_3^+ ion, 85° . The bipyramidal configuration of Ca_3Cl_5^+ (D_{3h}), in contrast to that of Ca_2Cl_3^+ , appears flattened due to a large horizontal hexagonal fragment. In the vibrational spectra of Ca_3Cl_5^+ , no low frequencies are observed; the lowest one is about 100 cm^{-1} . The most intensive bands correspond to doubly degenerated modes ω_7 and ω_8 : the mode $\omega_7(E) = 324\text{ cm}^{-1}$ is the antisymmetrical Ca– Cl_h stretching and $\omega_8(E) = 257\text{ cm}^{-1}$ is the combination of Ca– Cl_h stretching and bending Ca– Cl_h –Ca vibrations. The intensive mode $\omega_5(A_2'') = 268\text{ cm}^{-1}$ corresponds to the Ca– Cl_v stretching vibration.

Table 3. Properties of the pentaatomic Ca_2Cl_3^+ ion of D_{3h} symmetry

Property ^a	DFT B2	MP2 B2
$R_e(\text{Ca}-\text{Cl})$	2.600	2.613
$\alpha_e(\text{Cl}-\text{Ca}-\text{Cl})$	85.0	85.0
$-E$	2735.94286	2733.41284
$\omega_1(A_1')$	324	348
$\omega_2(A_1')$	194	199
$\omega_3(A_2'')$	280 (3.93)	284 (4.26)
$\omega_4(E')$	296 (5.58)	304 (5.76)
$\omega_5(E')$	125 (0.88)	122 (1.02)
$\omega_6(E')$	190	210

^a For the Ca_2Cl_3^+ (D_{3h}) the vibrational representation is $\Gamma = 2A_1' + A_2'' + 2E' + E''$

3.5 Undecaatomic Positive Ion Ca_4Cl_7^+

The properties of Ca_4Cl_7^+ were computed by DFT and MP2 methods with McLean-Chandler basis set (B1). Two configurations of the ion were considered, the polyhedron of C_{2v} symmetry and chain with three cycles lying in mutually perpendicular planes of C_{2v} symmetry. The latter configuration, with energy higher than the former by $210\text{ kJ}\cdot\text{mol}^{-1}$ (DFT) and $234\text{ kJ}\cdot\text{mol}^{-1}$ (MP2), appeared to be nonequilibrium as associated with imaginary frequencies. The polyhedron of

C_{2v} symmetry was confirmed to be equilibrium (Fig. 7).

This structure may be considered as composed of the Ca_2Cl_3^+ bipyramidal moiety and two CaCl_2 molecules attached. The Ca atoms of CaCl_2 molecules link to the Cl atoms of the base of the Ca_2Cl_3^+ bipyramid and Cl atoms are attached to the vertex Ca atoms of the bipyramid. Two Ca atoms and three Cl atoms lie in one plane forming a pentagonal ring. The attachment of two CaCl_2 molecules results in a distortion the original bipyramid Ca_2Cl_3^+ , and the Ca_v – Cl_h internuclear separations become nonequivalent as well as valence angles Cl_h – Ca_v – Cl_h . The dipole moment of the ion Ca_4Cl_7^+ appears due to both the attachment of CaCl_2 molecules and distortion of the bipyramidal Ca_2Cl_3^+ fragment and directs along the C_2 axis (axis z in Fig. 7). The parameters of the Ca_4Cl_7^+ ion are given in Table 6. There are six types of equilibrium internuclear distances obtained, $R_{e1}(\text{Ca}_v$ – $\text{Cl}_h)$, $R_{e2}(\text{Ca}_v$ – $\text{Cl}_{h1})$, $R_{e3}(\text{Ca}_v$ – $\text{Cl})$, $R_{e4}(\text{Ca}$ – $\text{Cl})$, $R_{e5}(\text{Ca}$ – $\text{Cl}_{h1})$ and $R_{e6}(\text{Ca}$ – $\text{Cl}_h)$. The equilibrium angles are of four types, $\alpha_e(\text{Cl}_h$ – Ca_v – $\text{Cl}_h)$, $\alpha'_e(\text{Cl}_h$ – Ca_v – $\text{Cl}_{h1})$, $\beta_e(\text{Cl}$ – Ca_v – $\text{Cl})$ and $\gamma_e(\text{Cl}$ – Ca – $\text{Cl})$. The respective values of the geometrical parameters, dipole moment, and vibrational frequencies found by two methods, DFT B1 and MP2 B1, agree well with each other.

The theoretical IR spectrum is presented in Fig. 8. As is seen, the most intensive bands are observed for ω_1 , ω_4 , ω_{15} , ω_{16} , ω_{19} , ω_{22} , and ω_{24} frequencies. The modes $\omega_1(A_1) = 267\text{ cm}^{-1}$, $\omega_{15}(B_1) = 297\text{ cm}^{-1}$, and $\omega_{16}(B_1) = 263\text{ cm}^{-1}$ correspond to the stretching vibrations of the attached CaCl_2 molecules and bipyramidal fragment Ca_2Cl_3^+ ; $\omega_{19}(B_1) = 160\text{ cm}^{-1}$ is assigned to the bending mode of Ca–Cl bonds formed between Ca atoms in the CaCl_2 molecules attached and Cl atoms in the Ca_2Cl_3^+ bipyramid. The highest intensity band $\omega_{22}(B_2) = 332\text{ cm}^{-1}$ relates to the stretching vibration of CaCl_2 moieties. Overlapping of two bands $\omega_4(A_1)$ and $\omega_{24}(B_2)$ gives the peak at 215 cm^{-1} , which is stretching vibration of atoms in the pentagonal ring, and the stretching of the bipyramidal moiety.

3.6Tetradecanatomic Positive Ion Ca_5Cl_9^+

Opposite to the ionic clusters considered above, the tetradecanatomic Ca_5Cl_9^+ ion was not detected experimentally. Nevertheless the formation of this ion is feasible. The properties of Ca_5Cl_9^+ were computed by DFT B1 method only.

Two configurations of the ion were considered, the polyhedron of D_{3h} symmetry and the chain structure composed of four cycles in mutually perpendicular planes, C_{2v} symmetry. The latter configuration, with energy higher by $255 \text{ kJ}\cdot\text{mol}^{-1}$

than the former, appeared to be nonequilibrium as associated with imaginary frequencies. The polyhedral structure of the D_{3h} symmetry was confirmed to be equilibrium (Fig. 8). The parameters are given in Table 6.

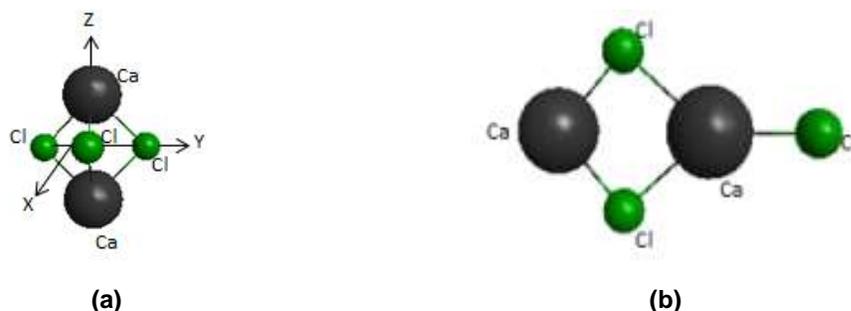


Fig. 4. The equilibrium geometrical structures of the ion Ca_2Cl_3^+ : (a) bipyramidal, D_{3h} symmetry; (b) kite shaped, C_{2v} symmetry

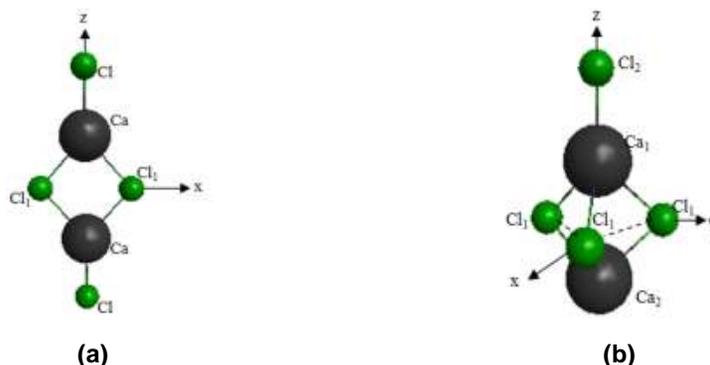


Fig. 5. Equilibrium geometrical structures of the Ca_2Cl_4 dimer molecule: (a) D_{2h} symmetry; (b) C_{3v} symmetry

Table 4. Properties of the dimer Ca_2Cl_4 molecule (D_{2h} and C_{3v} structures)

Property ^a	DFT B2	MP2 B2	Property ^a	DFT B2	MP2 B2
Ca_2Cl_4 (D_{2h})			Ca_2Cl_4 (C_{3v})		
$R_{e1}(\text{Ca}-\text{Cl}_1)$	2.648	2.652	$R_{e1}(\text{Ca}_1-\text{Cl}_1)$	2.778	2.763
$R_{e2}(\text{Ca}-\text{Cl})$	2.444	2.469	$R_{e2}(\text{Ca}_2-\text{Cl}_1)$	2.545	2.559
$\alpha_e(\text{Cl}_1-\text{Ca}-\text{Cl}_1)$	87.0	86.5	$R_{e3}(\text{Ca}_1-\text{Cl}_2)$	2.458	2.483
$-E$	3196.45082	3193.46324	$\alpha_e(\text{Ca}_1-\text{Cl}_1-\text{Ca}_2)$	76.2	76.4
ΔE_{iso}	0.0	0.0	ΔE_{iso}	-4.1	-21.7
$\omega_1(A_g)$	402	402	$-E$	3196.45235	3193.47149
$\omega_2(A_g)$	235	242	$\omega_1(A_1)$	382 (3.04)	385 (2.70)
$\omega_3(A_g)$	106	105	$\omega_2(A_1)$	324 (2.32)	327 (2.57)
$\omega_4(B_{1g})$	228	237	$\omega_3(A_1)$	195 (1.22)	206 (1.02)
$\omega_5(B_{1g})$	61	65	$\omega_4(A_1)$	152 (0.01)	155 (0.04)
$\omega_6(B_{2g})$	40	56	$\omega_5(E)$	302 (4.94)	311 (4.94)
$\omega_7(B_{1u})$	95 (1.73)	95 (1.90)	$\omega_6(E)$	157 (0.56)	182 (0.60)
$\omega_8(B_{1u})$	20 (0.39)	24 (0.41)	$\omega_7(E)$	115 (0.79)	115 (0.91)
$\omega_9(B_{2u})$	279 (2.67)	284 (2.78)	$\omega_8(E)$	50 (0.08)	50 (0.10)
$\omega_{10}(B_{2u})$	40 (0.47)	41 (0.56)			
$\omega_{11}(B_{3u})$	382 (9.80)	385 (8.90)			
$\omega_{12}(B_{3u})$	226 (0.86)	231 (0.57)			

^a For the Ca_2Cl_4 molecule the vibrational representations are $\Gamma = 3A_g + 2B_{1g} + B_{2g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$ (D_{2h}) and $\Gamma = 4A_1 + 4E$ (C_{3v}); ΔE_{iso} is the energy of the isomerization reaction Ca_2Cl_4 (D_{2h}) = Ca_2Cl_4 (C_{3v}) in $\text{kJ}\cdot\text{mol}^{-1}$

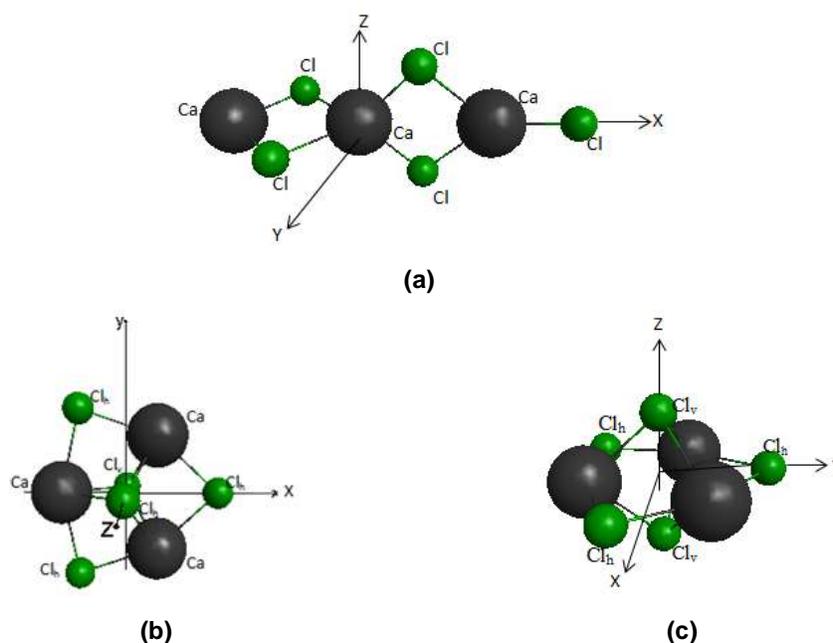


Fig. 6. Equilibrium geometrical structure of the Ca_3Cl_5^+ ion: (a) two fragments are in mutually perpendicular planes, C_{2v} symmetry; (b) bipyramidal structure, D_{3h} , top view; (c) bipyramidal structure, D_{3h} , side view

Table 5. Properties of the octaatomic $\text{Ca}_3\text{Cl}_5^+(D_{3h})$ ion

Property ^a	DFT B2	MP2 B2
$R_{e1}(\text{Ca}-\text{Cl}_h)$	2.644	2.650
$R_{e2}(\text{Ca}-\text{Cl}_v)$	2.721	2.715
$\alpha_e(\text{Ca}-\text{Cl}_h-\text{Ca})$	84.4	84.1
$\beta_e(\text{Ca}-\text{Cl}_v-\text{Ca})$	81.5	81.7
$-E$	4334.22743	4330.22806
$\omega_1 (A_1')$	281	319
$\omega_2 (A_1')$	226	280
$\omega_3 (A_1')$	213	252
$\omega_4 (A_1')$	176	120
$\omega_5 (A_2'')$	253 (2.80)	268 (2.90)
$\omega_6 (A_2'')$	103 (0.62)	104 (0.75)
$\omega_7 (E')$	312 (9.11)	324 (8.45)
$\omega_8 (E')$	242 (3.69)	257 (4.90)
$\omega_9 (E')$	154 (0.06)	163 (0.13)
$\omega_{10} (E')$	144 (0.42)	148 (0.32)
$\omega_{11} (E'')$	178	196
$\omega_{12} (E'')$	97	99

^a For the $\text{Ca}_3\text{Cl}_5^+ (D_{3h})$ the vibrational representation is $\Gamma = 4A_1' + 2A_2'' + 4E' + 2E''$

This structure may be considered as composed of the Ca_2Cl_3^+ bipyramidal moiety and three CaCl_2 molecules attached. There are four types of Ca-Cl internuclear distances, the longest is $R_{e1}(\text{Ca}-\text{Cl}_h) = 3.114 \text{ \AA}$ in the bipyramid Ca_2Cl_3^+ , the shortest is $R_{e2}(\text{Ca}_h-\text{Cl}) = 2.669 \text{ \AA}$ in the

CaCl_2 molecules attached. A hexagonal ring is formed by three Ca atoms and three Cl atoms lying in one plane in the middle of the polyhedron Ca_5Cl_9^+ ; there are six equivalent Ca_h-Cl_h bonds with internuclear separation 2.803 \AA and three acute bond angles $\text{Cl}_h-\text{Ca}_h-\text{Cl}_h$ equal to 76.5° . The ion Ca_5Cl_9^+ possesses a perfect and compact structure and looks like a sandwich of two slightly nonplanar CaCl_3 fragments on the top and bottom and Ca_3Cl_3 hexagon between. In the CaCl_3 fragments, the internuclear distance Ca-Cl is 2.755 \AA .

The theoretical IR spectrum is presented in Fig. 9. The most intensive bands are observed for ω_9 , ω_{11} , ω_{12} , ω_{13} , ω_{14} , and ω_{16} frequencies. The mode $\omega_9 (A'') = 338 \text{ cm}^{-1}$ is the stretching vibration of CaCl_2 fragments attached, that is close to the similar vibration at 332 cm^{-1} in Ca_4Cl_7^+ ion. The frequencies $\omega_{11} (A'')$, and $\omega_{16} (E')$, both equal to 135 cm^{-1} , correspond to bending vibration of the hexagonal ring. The frequency $\omega_{12} (A'') = 111 \text{ cm}^{-1}$ is the bending of the top and bottom CaCl_3 fragments. The vibration modes $\omega_{13} (E) = 282 \text{ cm}^{-1}$, and $\omega_{14} (E) = 264 \text{ cm}^{-1}$ correspond to the stretching vibrations of the attached CaCl_2 molecules and bipyramidal Ca_2Cl_3^+ moiety; these modes are similar to the vibrations 297 cm^{-1} and 263 cm^{-1} in the Ca_4Cl_7^+ ion.

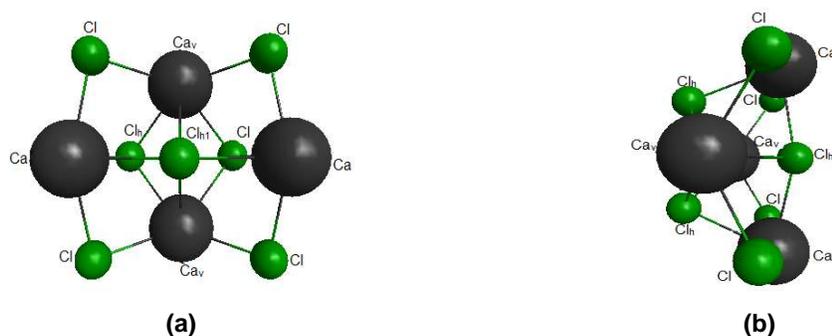


Fig. 7. Equilibrium geometrical structure of the Ca_4Cl_7^+ , C_{2v} symmetry: (a) top view; (b) side view

Table 6. Properties of the undecaatomic Ca_4Cl_7^+ ion of C_{2v} symmetry

Property ^a	DFT B1	MP2 B1
$R_{e1}(\text{Ca}_v\text{-Cl}_h)$	2.870	2.867
$R_{e2}(\text{Ca}_v\text{-Cl}_{h1})$	2.944	2.945
$R_{e3}(\text{Ca}_v\text{-Cl})$	2.738	2.741
$R_{e4}(\text{Ca}\text{-Cl})$	2.681	2.685
$R_{e5}(\text{Ca}\text{-Cl}_{h1})$	2.888	2.887
$R_{e6}(\text{Ca}\text{-Cl}_h)$	2.778	2.785
$\alpha_e(\text{Cl}_h\text{-Ca}_v\text{-Cl}_h)$	72.6	72.9
$\alpha'_e(\text{Cl}_h\text{-Ca}_v\text{-Cl}_{h1})$	76.4	73.5
$\beta_e(\text{Cl}\text{-Ca}_v\text{-Cl})$	118.1	117.5
$\gamma_e(\text{Cl}\text{-Ca}\text{-Cl})$	156.5	155.8
$-E$	5932.21088	5925.86678
μ_e	5.66	5.65
$\omega_1 (A_1)$	261 (4.43)	267 (4.94)
$\omega_2 (A_1)$	248 (0.01)	252 (0.01)
$\omega_3 (A_1)$	220 (0.65)	225 (0.52)
$\omega_4 (A_1)$	209 (1.20)	215 (1.49)
$\omega_5 (A_1)$	191 (0.04)	195 (0.04)
$\omega_6 (A_1)$	160 (0.12)	164 (0.16)
$\omega_7 (A_1)$	127 (0.31)	132 (0.38)
$\omega_8 (A_1)$	101 (0.47)	105 (0.46)
$\omega_9 (A_1)$	80 (0.03)	83 (0.04)
$\omega_{10} (A_2)$	326	330
$\omega_{11} (A_2)$	259	266
$\omega_{12} (A_2)$	162	167
$\omega_{13} (A_2)$	116	121
$\omega_{14} (A_2)$	67	70
$\omega_{15} (B_1)$	291 (5.35)	297 (5.71)
$\omega_{16} (B_1)$	257 (2.92)	263 (3.02)
$\omega_{17} (B_1)$	207 (0.05)	211 (0.05)
$\omega_{18} (B_1)$	188	194
$\omega_{19} (B_1)$	155 (1.10)	160 (1.20)
$\omega_{20} (B_1)$	143 (0.39)	148 (0.40)
$\omega_{21} (B_1)$	99 (0.60)	104 (0.67)
$\omega_{22} (B_2)$	327 (6.36)	332 (6.76)
$\omega_{23} (B_2)$	223 (0.79)	228 (0.76)
$\omega_{24} (B_2)$	208 (1.88)	215 (2.10)
$\omega_{25} (B_2)$	160 (0.06)	167 (0.03)
$\omega_{26} (B_2)$	136 (0.55)	140 (0.67)
$\omega_{27} (B_2)$	77	80

^a For Ca_4Cl_7^+ (C_{2v}) the vibrational representation is $\Gamma = 9A_1 + 5A_2 + 7B_1 + 6B_2$

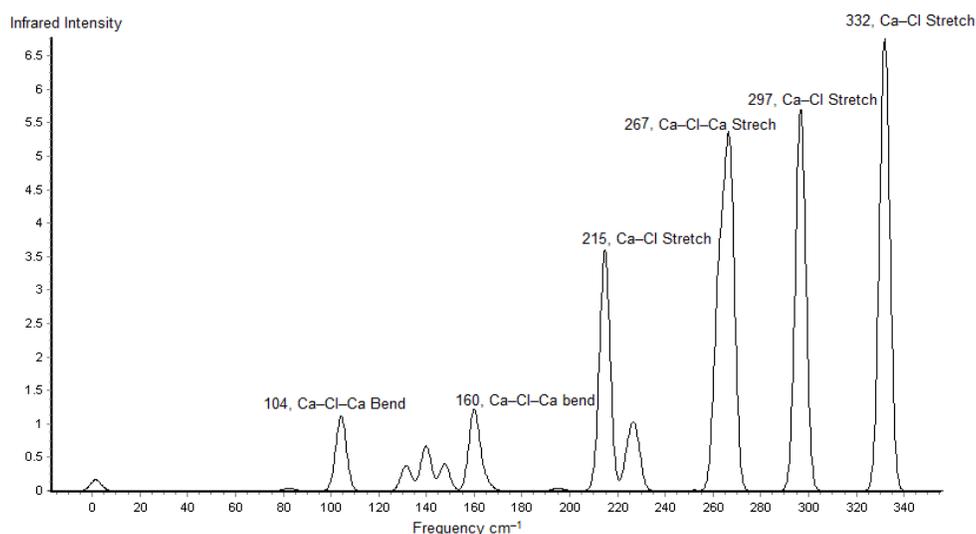


Fig. 8A. The theoretical IR spectrum of the undecaatomic Ca_4Cl_7^+ ion (C_{2v})

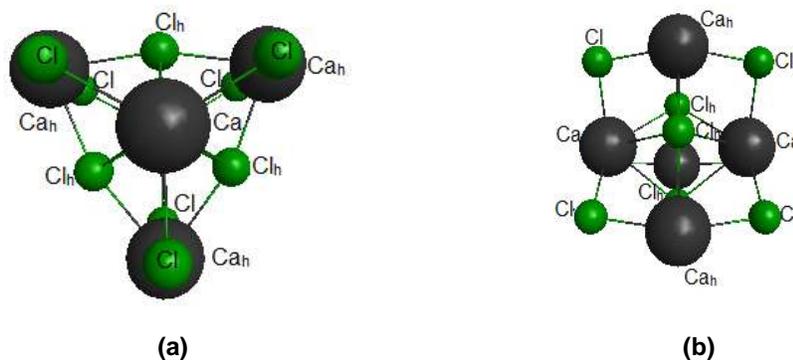


Fig. 8. Equilibrium geometrical structure of the Ca_5Cl_9^+ of D_{3h} symmetry: (a) top view (b) side view

Table 7. Properties of the tetradecanatomic Ca_5Cl_9^+ ion of D_{3h} symmetry

Property ^a	DFT B1	Property ^a	DFT B1
$R_{e1}(\text{Ca}-\text{Cl}_h)$	3.114	$\omega_{10}(A'')$	202 (0.12)
$R_{e2}(\text{Ca}_h-\text{Cl})$	2.669	$\omega_{11}(A'')$	135 (1.87)
$R_{e3}(\text{Ca}_h-\text{Cl}_h)$	2.803	$\omega_{12}(A'')$	111 (1.28)
$R_{e4}(\text{Ca}-\text{Cl})$	2.755	$\omega_{13}(E')$	282 (13.07)
$\alpha_e(\text{Ca}_h-\text{Cl}_h-\text{Cl}_h)$	163.5	$\omega_{14}(E')$	264 (4.75)
$\beta(\text{Cl}_h-\text{Ca}_h-\text{Cl}_h)$	76.5	$\omega_{15}(E')$	201 (0.01)
$-E$	7530.41323	$\omega_{16}(E')$	135 (5.20)
$\omega_1(A')$	233	$\omega_{17}(E')$	86 (0.50)
$\omega_2(A')$	227	$\omega_{18}(E')$	71 (0.01)
$\omega_3(A')$	224	$\omega_{19}(E')$	330
$\omega_4(A')$	181	$\omega_{20}(E')$	245
$\omega_5(A')$	161	$\omega_{21}(E')$	177
$\omega_6(A')$	100	$\omega_{22}(E')$	153
$\omega_7(A')$	93	$\omega_{23}(E')$	98
$\omega_8(A')$	71	$\omega_{24}(E')$	36
$\omega_9(A'')$	338 (8.65)		

^a For Ca_5Cl_9^+ (D_{3h}) the vibrational representation is $\Gamma = 8A' + 4A'' + 6E' + 6E''$

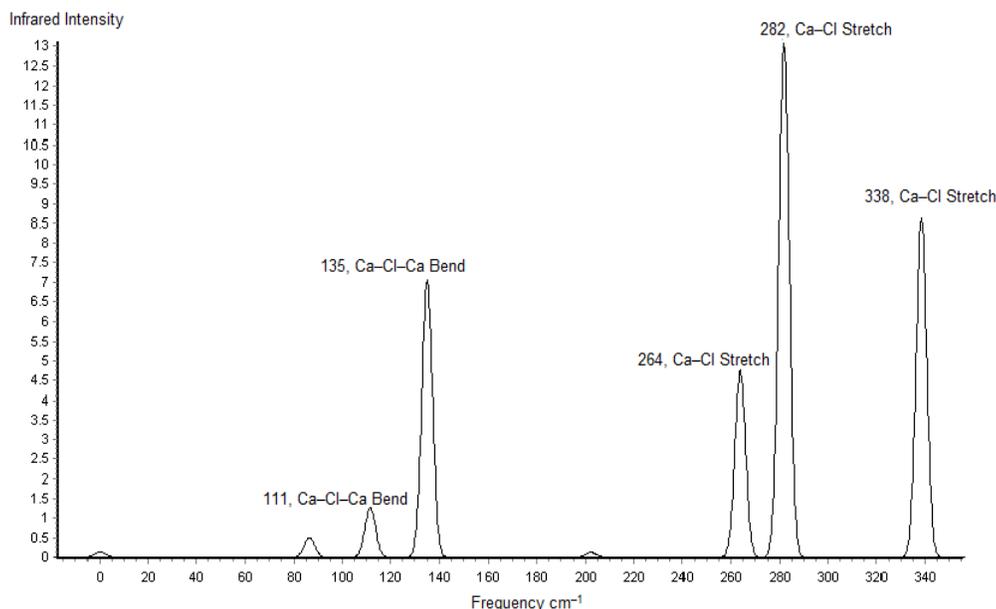


Fig. 9. The theoretical IR spectrum of Ca₅Cl₉⁺ ion (D_{3h})

4. CONCLUSION

The cluster ions CaCl⁺, CaCl₃⁻, Ca₂Cl₃⁺, Ca₃Cl₅⁺, and Ca₄Cl₇⁺ have been detected earlier in the equilibrium vapour by high temperature mass spectrometry technique. The formation of the heavier cluster Ca₅Cl₉⁺ was predicted. The geometrical structure and vibrational spectra of the ions were determined using the DFT and MP2 methods. The structures of the positive ions were designed through the consequent attachment of CaCl₂ molecule to CaCl⁺ ion. Alternative configurations were considered but no isomers revealed. The equilibrium geometrical structures of the ions Ca₂Cl₃⁺, Ca₃Cl₅⁺, and Ca₅Cl₉⁺ confirmed to be compact and rigid of a perfect shape and high symmetry. The equilibrium structure of the ion Ca₄Cl₇⁺ is of lower symmetry, and therefore lower stability of the ion regarding dissociation with CaCl₂ molecule elimination may be expected.

ACKNOWLEDGEMENT

The authors are grateful to BG Company for sponsorship and NM-AIST for support of this research. We are also pleased to acknowledge the valuable assistance and service by the School of Computational and Communicational Science and Engineering at NM-AIST.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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