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

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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.

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ABSTRACT

Geometrical structure and vibrational spectra for CaCl³⁻, Ca₂Cl³⁺, Ca₃Cl⁵⁺, Ca₄Cl⁷⁺, and Ca₅Cl⁹⁺ ions have been studied by employing density functional theory and the second order Möller–Plesset perturbation theory. The equilibrium geometrical structures are as follows: the planar $D_{3h}$ for CaCl³⁻, triple-bridged bipyramid $D_{3h}$ for Ca₂Cl³⁺, hexa-bridged bipyramid $D_{3h}$ for Ca₃Cl⁵⁺, polyhedral $C_{2v}$ for Ca₄Cl⁷⁺, and polyhedral $D_{3h}$ for Ca₅Cl⁹⁺. No isomers have been confirmed to exist.

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

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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 MX₂, 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, MX₃⁻ (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 [(CaCl₂)n + CaCl]⁺ and [(CaCl₂)n+ Cl]⁻ in vapour phase [7]. The ion-molecular equilibria involving CaCl⁺, Ca₂Cl⁻, Ca₃Cl⁻, and Ca₄Cl⁻ 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 Ba₂Cl₆⁺, Ba₃Cl₆⁺, Ba₄Cl₆⁺ and BaCl₀ 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⁺, Ca₂Cl⁻, Ca₃Cl⁻, Ca₄Cl⁺, and Ca₅Cl⁺ 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 CaCl₂ to analyze how the basis set and the computational method applied affect the results. The properties of the ions CaCl⁺, Ca₂Cl⁻, and Ca₃Cl⁻ 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 Ca₄Cl⁺ and only DFT B1 for the heaviest Ca₅Cl⁺ 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 CaCl₂

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 $R_e$(Ca–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 $R_e$(Ca–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 = Ca, Sr, Ba; X = F, Cl, 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 | DFT B1 | MP2 B1 | DFT B2 | MP2 B2 | Reference |
|----------|--------|--------|--------|--------|-----------|
| CaCl | | | | | |
| $R_e$(Ca–Cl) | 2.563 | 2.563 | 2.426 | 2.426 | 2.437 [36], 2.439 [37] |
| $\omega_e$ | 331 | 373 | 1137.79212 | 1136.58079 | 1137.86201 | 1136.80828 |
| $\mu_e$ | 8.53 | 4.05 | 367.53 [37], 368 [38] |
| $E_A$ | 1.29 | 1.23 | 6.22 | 6.01 | 5.86±0.07 [39,38] |
| $|E_{ad}|$ | 6.27 | 5.68 | 6.08 | 5.97 | 6.01±0.10 [40,38] |
| CaCl$^+$ | | | | | |
| $R_e$(Ca–Cl) | 2.465 | 2.470 | 2.314 | 2.350 | |
| $\omega_e$ | 409 (1.51) | 414 (1.86) | 454 (2.53) | 441 (2.70) | |
| $\mu_e$ | 8.1 | 9.3 | 5.4 | 6.8 | |
| CaCl$_2$ | | | | | |
| $R_e$(Ca–Cl) | 2.526 | 2.531 | 2.460 | 2.482 | 2.483 [12], 2.483 [13], 2.455 [14b] |
| $\alpha_e$(Cl–Ca–Cl), degrees | 180 | 180 | 180 | 180 | 180 [12–14b, 41] |
| $|E_{ad}|$ | 1598.10447 | 1596.38062 | 1598.18823 | 1596.68708 | |
| $|E_{ad}|$ | 273 | 279 | 282 | 276 | 243 [14], 238 [16] |
| $\omega_e$ (Π$_u$) | 61 | 68 | 27 | 37 | 69 [12], 64 [14], 66 [42], 72 [42] |
| $\omega_e$ (Σ$^+ _g$) | 439 | 446 | 423 | 422 | 402 [14], 403 [42], 414 [43], 395 [16], 397 [42], 394 [43] |
| $|E_{ad}|$ | 9.74 | 9.58 | 9.65 | | 10.5±0.3 [44,38], 10.2 [45,38] |

*Here and hereafter in Tables 2–7 $R_e$(Ca–Cl) is the equilibrium internuclear distance, Å; valence angle $\alpha_e$(Cl–Ca–Cl), degrees; $\omega_e$ is the normal mode frequency, cm$^{-1}$; $\mu_e$ is the dipole moment, D; $|E|$ is the ionization energy, eV
The calculated vibrational frequencies for CaCl and CaCl$_2$ 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 $\omega_e$ 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 $\omega_e$ increase.

In the vibrational spectrum of CaCl$_2$ molecule (Table 1) the valence frequencies calculated by four methods agree well between each other and do not contradict to the experimental values, being overrated, by ~5–12%. For the deformational frequency $\omega_2$, 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 $\omega_1$, $\omega_2$, and $\omega_3$ 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 $\omega_2$, 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].

![Fig. 1. Internuclear distance $R_e$(Å) in the CaCl, CaCl$^+$, BaCl [25], and CaCl$_2$ versus method of determination](image1)

![Fig. 2. Frequency of vibration $\omega_e$(cm$^{-1}$) in the CaCl, CaCl$^+$, and BaCl$^+$ [25] versus method of determination](image2)
The ionization energies of neutral molecules have been computed; the vertical and adiabatic. Adiabatic ionization energy ($\langle IE_{ad}\rangle$) was obtained as the difference between the total energies of neutral and ionized particles with the geometry optimized for each species. The values of $\langle IE_{ad}\rangle$ for CaCl calculated with DFT B2 are in good agreement with experimental data [38,39]. Vertical ionization energy ($\langle IE_{vert}\rangle$) 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 CaCl$_2$, and accepted the same for positive ions, CaCl$^+$ and CaCl$_2^+$. The values of $\langle IE_{vert}\rangle$ computed by DFT B2 and MP2 B2 for CaCl and CaCl$_2$ 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 CaCl$_3^-$ and Neutral Species CaCl$_3$

The geometrical structure of the CaCl$_3^-$ ion was found to be planar of $D_{3h}$ symmetry. For the neutral CaCl$_3$ 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 CaCl$_3^-$ ion is $^1A_1^-$, and that of the neutral CaCl$_3$ is $^2B_2$. The equilibrium geometrical configurations of the CaCl$_3^-$ ion and CaCl$_3$ 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 CaCl$_3$ neutral particle is in good accordance between both methods and theoretical value [22].

### 3.3 Pentaatomic Positive Ion Ca$_2$Cl$_5^+$

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 Ca$_2$Cl$_5^+$, 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 Ca$_2$Cl$_5^+$ 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 Ca$_2$Cl$_5^+$ ion does not contain low frequencies. Thus the structure of this ion is compact and rigid. The most intensive bands are $\omega_3$ ($A_1^-$) = 284 cm$^{-1}$ and $\omega_4$ ($E$) = 304 cm$^{-1}$ (MP2 B2), which correspond to antisymmetrical stretching Ca-Cl vibrations; the mode $\omega_5$ ($E$) = 122 cm$^{-1}$ is bending Cl-Ca-Cl vibration.

If compare the parameters of the Ca$_2$Cl$_5^+$ ion with those of the similar Ba$_2$Cl$_5^+$ 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 Ca$_2$Cl$_5^+$ ion to that of the neutral dimer molecule Ca$_2$Cl$_4$. The same theoretical approaches, DFT B2 and MP2 B2, were applied to compute the molecular parameters of the dimeric molecule Ca$_2$Cl$_4$. Two isomeric configurations were proved to exist: the planar cyclic configuration of $D_{3h}$ 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 Ca$_2$Cl$_5^+$, compared to dimer molecule Ca$_2$Cl$_4$ 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 Ca$_2$Cl$_4$ molecule, low deformational frequencies are found, $\omega_8 = 20$ cm$^{-1}$ (DFT B2) and 24 cm$^{-1}$ (MP2 B2), $\omega_{10} = 40$ 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, $\omega_8 = 50$ 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 kJ mol$^{-1}$ (DFT B2) and 22 kJ 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 kJ mol$^{-1}$ (DFT B1) and 13 kJ 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 kJ 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$_3$Cl$_5^+$

Two possible configurations of the ions were considered; bipyramidal of $D_{3h}$ symmetry and $C_{2v}$ symmetry, in the latter two Ca$_2$Cl$_2$ cyclic fragments are located in the mutually perpendicular planes (Fig. 6). The two-cycled configuration was found of higher energy, by 193 kJ 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 | DFT B2 | MP2 B2 | Reference [22]$^b$ |
|----------|--------|--------|------------------|
| CaCl$_3$ $^-$ ($D_{3h}$, $A_1'$) | | |
| $R_e$(Ca–Cl) | 2.547 | 2.542 | 2.566 |
| $\omega_8$ ($A_1'$) | 239 | 213 | 242 |
| $\omega_9$ ($A_2''$) | 93 (1.31) | 96 (1.41) | 100 |
| $\omega_{10}$ ($E$) | 330 (6.83) | 341 (6.42) | 344 |
| $\omega_{11}$ ($E$) | 76 (0.26) | 76 (0.36) | 80 |
| CaCl$_3$ ($C_{2v}$, $B_2$) | | |
| $R_e$(Ca–Cl) | 2.448 | 2.448 | 2.473 |
| $\alpha_{\text{d}}$(Cl–Ca–Cl) | 61.3 | 61.3 | 62.1 |
| --E | 2058.37900 | 2056.42069 | 2056.10365 |
| $EA_{ad}$ | 5.34 | 5.58 | 5.37 |
| $\omega_1$ ($A_1$) | 403 (4.82) | 412 | 412 |
| $\omega_2$ ($A_1$) | 262 (0.01) | 260 | 260 |
| $\omega_3$ ($A_1$) | 184 (0.12) | 181 | 181 |
| $\omega_4$ ($B_1$) | 43 (1.11) | 38 | 38 |
| $\omega_5$ ($B_2$) | 227 (0.16) | 216 | 216 |
| $\omega_6$ ($B_2$) | 49 (0.57) | 49 | 49 |

$^a$ Here and hereafter, the values given in parentheses near the frequencies are infrared intensities in D$^2$amu$^{-1}$Å$^{-2}$. 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$_5$ $^-$ 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 \( \text{Ca}_2\text{Cl}_5^+ \) \((D_{3h})\) are reported in Table 5. There are two kinds of equilibrium internuclear distances \( \text{Ca}–\text{Cl} \): \( R_e(\text{Ca}–\text{Cl}_i) \) and \( R_e(\text{Ca}–\text{Cl}_h) \) where \( \text{Cl}_i \) and \( \text{Cl}_h \) denote the chlorine atoms in the vertex and horizontal plane of the bipyramid, respectively. The basis of the bipyramid is hexagon formed by three \( \text{Ca} \) and three \( \text{Cl} \) atoms. The internuclear separation between two \( \text{Cl}_h \) atoms (5.182 Å, MP2 B2) is much larger than that between two \( \text{Cl}_i \) (3.558 Å, MP2 B2), the \( \text{Ca}–\text{Cl}_i \) bond being shorter than \( \text{Ca}–\text{Cl}_h \) one, by 0.07–0.08 Å. The bond angle at the vertex of bipyramid is acute, \( 3.558 \) Å, MP2 B2), the \( \text{Ca}–\text{Cl}_i \) bond being shorter than \( \text{Ca}–\text{Cl}_h \) one, by 0.07–0.08 Å. The bond angle at the vertex of bipyramid is acute, \( 82^\circ \), close to that in the \( \text{Ca}_3\text{Cl}_5^+ \) ion, \( 85^\circ \). The bipyramidal configuration of \( \text{Ca}_2\text{Cl}_5^+ \) \((D_{3h})\), in contrast to that of \( \text{Ca}_2\text{Cl}_5^+ \), appears flattened due to a large horizontal hexagonal fragment. In the vibrational spectra of \( \text{Ca}_3\text{Cl}_5^+ \), no low frequencies are observed; the lowest one is about \( 100 \) cm\(^{-1}\). The most intensive bands correspond to doubly degenerated modes \( \omega_7 \) and \( \omega_5 \); the mode \( \omega_7(E) = 324 \) cm\(^{-1}\) is the antisymmetrical \( \text{Cl}-\text{Ca}–\text{Cl} \) stretching and \( \omega_5(E) = 257 \) cm\(^{-1}\) is the combination of \( \text{Ca}–\text{Cl}_i \) stretching and bending \( \text{Ca}–\text{Cl}_i–\text{Ca} \) vibrations. The intensive mode \( \omega_5 (A^e_2) = 268 \) cm\(^{-1}\) corresponds to \( \text{Ca}–\text{Cl} \) stretching vibration.

### Table 3. Properties of the pentatomic \( \text{Ca}_2\text{Cl}_5^+ \) ion of \( D_{3h} \) symmetry

| Property* | DFT B2 | MP2 B2 |
|-----------|--------|--------|
| \( R_e(\text{Ca}–\text{Cl}) \) | 2.600 | 2.613 |
| \( \alpha(\text{Cl}–\text{Ca}–\text{Cl}) \) | 85.0 | 85.0 |
| \( -E \) | 2735.94286 | 2733.41284 |
| \( \omega_1 (A^i_1) \) | 324 | 348 |
| \( \omega_2 (A^i_1) \) | 194 | 199 |
| \( \omega_3 (A^e_2) \) | 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 |

*For the \( \text{Ca}_3\text{Cl}_5^+ \) \((D_{3h})\) the vibrational representation is \( \Gamma = 2A^i_1 + 2A^e_2 + 2E' + E'' \)

### 3.5 Undecaatomic Positive Ion \( \text{Ca}_4\text{Cl}_7^+ \)

The properties of \( \text{Ca}_4\text{Cl}_7^+ \) 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 \( 210 \) kJ mol\(^{-1}\) (DFT) and \( 234 \) kJ 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 \( \text{Ca}_2\text{Cl}_5^+ \) bipyramidal moiety and two \( \text{CaCl}_2 \) molecules attached. The \( \text{Ca} \) atoms of \( \text{CaCl}_2 \) molecules link to the \( \text{Cl} \) atoms of the base of the \( \text{Ca}_2\text{Cl}_5^+ \) bipyramidal and \( \text{Cl} \) atoms are attached to the vertex \( \text{Ca} \) atoms of the bipyramid. Two \( \text{Ca} \) atoms and three \( \text{Cl} \) atoms lie in one plane forming a pentagonal ring. The attachment of two \( \text{CaCl}_2 \) molecules results in a distortion the original bipyramidal \( \text{Ca}_2\text{Cl}_5^+ \), and the \( \text{Ca}_2\text{Cl}_5^+ \) internuclear separations become nonequivalent as well as valence angles \( \text{Cl}–\text{Ca}–\text{Cl} \). The dipole moment of the ion \( \text{Ca}_2\text{Cl}_5^+ \) appears due to both the attachment of \( \text{CaCl}_2 \) molecules and distortion of the bipyramidal \( \text{Ca}_2\text{Cl}_5^+ \) fragment and directs along the \( C_2 \) axis (axis \( z \) in Fig. 7). The parameters of the \( \text{Ca}_2\text{Cl}_5^+ \) ion are given in Table 6. There are six types of equilibrium internuclear distances obtained, \( R_e(\text{Ca}–\text{Cl})_1 \), \( R_e(\text{Ca}–\text{Cl}_h) \), \( R_e(\text{Ca}–\text{Cl}_i) \), \( R_{o1}(\text{Ca}–\text{Cl})_1 \), \( R_{o1}(\text{Ca}–\text{Cl}_h) \), and \( R_{o1}(\text{Ca}–\text{Cl}_i) \). The equilibrium angles are of four types, \( \omega_1 (\text{Cl}–\text{Ca}–\text{Cl})_1 \), \( \omega_2 (\text{Cl}–\text{Ca}–\text{Cl})_1 \), \( \beta(\text{Cl}–\text{Ca}–\text{Cl})_1 \) and \( \gamma(\text{Cl}–\text{Ca}–\text{Cl})_1 \). 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 \( \omega_1 \), \( \omega_4 \), \( \omega_{15} \), \( \omega_{16} \), \( \omega_{19} \), \( \omega_{22} \), and \( \omega_{24} \) frequencies. The modes \( \omega_1 (A^i_1) = 267 \) cm\(^{-1}\), \( \omega_{15} (B^i_1) = 297 \) cm\(^{-1}\), and \( \omega_{16} (B^i_2) = 263 \) cm\(^{-1}\) correspond to the stretching vibrations of the attached \( \text{CaCl}_2 \) molecules and bipyramidal fragment \( \text{Ca}_2\text{Cl}_5^+ \); \( \omega_{19} (B^i_1) = 160 \) cm\(^{-1}\) is assigned to the bending mode of \( \text{Ca}–\text{Cl} \) bonds formed between \( \text{Ca} \) atoms in the \( \text{CaCl}_2 \) molecules attached and \( \text{Cl} \) atoms in the \( \text{Ca}_2\text{Cl}_5^+ \) bipyramid. The highest intensity band \( \omega_{22} (B^i_2) = 332 \) cm\(^{-1}\) relates to the stretching vibration of \( \text{CaCl}_2 \) moieties. Overlapping of two bands \( \omega_4 (A^i_1) \) and \( \omega_{24} (B^i_2) \) gives the peak at 215 cm\(^{-1}\), which is stretching vibration of atoms in the pentagonal ring, and the stretching of the bipyramidal moiety.

### 3.6 Tetraatomic Positive Ion \( \text{Ca}_3\text{Cl}_6^+ \)

Opposite to the ionic clusters considered above, the tetraatomic \( \text{Ca}_3\text{Cl}_6^+ \) ion was not detected experimentally. Nevertheless the formation of this ion is feasible. The properties of \( \text{Ca}_3\text{Cl}_6^+ \) 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 kJ 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$_2$Cl$_3^+$: (a) bipyramidal, $D_{3h}$ symmetry; (b) kite shaped, $C_{2v}$ symmetry](image)

![Fig. 5. Equilibrium geometrical structures of the Ca$_2$Cl$_4$ dimer molecule: (a) $D_{2h}$ symmetry; (b) $C_{3v}$ symmetry](image)

| Property$^a$ | DFT B2 | MP2 B2 | Property$^a$ | DFT B2 | MP2 B2 |
|-------------|--------|--------|-------------|--------|--------|
| Ca$_2$Cl$_4$ ($D_{2h}$) | | | Ca$_2$Cl$_4$ ($C_{3v}$) | | |
| $R_{e1}$(Ca–Cl$_1$) | 2.648 | 2.652 | $R_{e1}$(Ca$_1$–Cl$_1$) | 2.778 | 2.763 |
| $R_{e2}$(Ca–Cl) | 2.444 | 2.469 | $R_{e2}$(Ca$_2$–Cl$_1$) | 2.545 | 2.559 |
| $\alpha$$_4$(Cl$_1$–Ca–Cl$_1$) | 87.0 | 86.5 | $\alpha$$_4$(Ca$_1$–Cl$_1$–Ca$_2$) | 76.2 | 76.4 |
| $\Delta E_{iso}$ | 0.0 | 0.0 | $\Delta E_{iso}$ | -4.1 | -21.7 |
| $\omega$$_1$ (A$_g$) | 402 | 402 | $\omega$$_1$ (A$_1$) | 382 (3.04) | 385 (2.70) |
| $\omega$$_2$ (A$_g$) | 235 | 242 | $\omega$$_2$ (A$_1$) | 324 (2.32) | 327 (2.57) |
| $\omega$$_3$ (A$_g$) | 106 | 105 | $\omega$$_3$ (A$_1$) | 195 (1.22) | 206 (1.02) |
| $\omega$$_4$ (B$_1g$) | 228 | 237 | $\omega$$_4$ (A$_1$) | 152 (0.01) | 155 (0.04) |
| $\omega$$_5$ (B$_2g$) | 61 | 65 | $\omega$$_5$ (E) | 302 (4.94) | 311 (4.94) |
| $\omega$$_6$ (B$_2u$) | 40 | 46 | $\omega$$_6$ (E) | 157 (0.56) | 182 (0.60) |
| $\omega$$_7$ (B$_1u$) | 95 (1.73) | 95 (1.90) | $\omega$$_7$ (E) | 115 (0.79) | 119 (0.91) |
| $\omega$$_8$ (B$_2u$) | 20 (0.39) | 24 (0.41) | $\omega$$_8$ (E) | 50 (0.08) | 50 (0.10) |
| $\omega$$_9$ (B$_2u$) | 279 (2.67) | 284 (2.78) | |
| $\omega$$_{10}$ (B$_3u$) | 40 (0.47) | 41 (0.56) | |
| $\omega$$_{11}$ (B$_3u$) | 382 (9.80) | 385 (9.90) | |
| $\omega$$_{12}$ (B$_3u$) | 226 (0.86) | 231 (0.57) | |

$^a$ For the Ca$_2$Cl$_4$ molecule the vibrational representations are $\Gamma = 3A_g + 2B_{1g} + 2B_{2g} + 2B_{1u} + 2B_{2u} + 2B_{3u} (D_{2h})$ and $\Gamma = 4A_1 + 4E (C_{3v})$; $\Delta E_{iso}$ is the energy of the isomerization reaction Ca$_2$Cl$_4$ ($D_{2h}$) = Ca$_2$Cl$_4$ ($C_{3v}$) in kJ mol$^{-1}$.
Fig. 6. Equilibrium geometrical structure of the Ca$_3$Cl$_5^+$ 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 Ca$_3$Cl$_5^+(D_{3h})$ ion

| Property | DFT B2 | MP2 B2 |
|----------|--------|--------|
| $R_{e1}(\text{Ca–Cl}_h)$ | 2.644 | 2.650 |
| $R_{e2}(\text{Ca–Cl}_v)$ | 2.721 | 2.715 |
| $\alpha_{el}(\text{Ca–Cl}_h)$ | 84.4 | 84.1 |
| $\beta_{el}(\text{Ca–Cl}_v)$ | 81.5 | 81.7 |
| $\omega_1$ ($A'_1$) | 281 | 319 |
| $\omega_2$ ($A'_1$) | 226 | 280 |
| $\omega_3$ ($A'_1$) | 213 | 252 |
| $\omega_4$ ($A''_1$) | 176 | 120 |
| $\omega_5$ ($A''_1$) | 253 (2.80) | 268 (2.90) |
| $\omega_6$ ($A''_1$) | 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) |
| $\omega_{11}$ ($E''_1$) | 178 | 196 |
| $\omega_{12}$ ($E''_1$) | 97 | 99 |

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

This structure may be considered as composed of the Ca$_3$Cl$_5^+$ bipyramidal moiety and three 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$_3$Cl$_5^+$; there are six equivalent Ca–Cl$_h$ bonds with internuclear separation 2.803 Å and three acute bond angles Cl$_h$-Ca–Cl$_h$ equal to 76.5°. The ion Ca$_3$Cl$_5^+$ possesses a perfect and compact structure and looks like a sandwich of two slightly nonplanar CaCl$_2$ fragments on the top and bottom and Ca$_3$Cl$_3$ hexagon between. In the CaCl$_3$ fragments, the internuclear distance Ca–Cl is 2.755 Å.

The theoretical IR spectrum is presented in Fig. 9. The most intensive bands are observed for $\omega_9$, $\omega_{11}$, $\omega_{12}$, $\omega_{13}$, $\omega_{14}$, and $\omega_{16}$ frequencies. The mode $\omega_9$ ($A''$) = 338 cm$^{-1}$ is the stretching vibration of CaCl$_2$ fragments attached, that is close to the similar vibration at 332 cm$^{-1}$ in Ca$_4$Cl$_7^+$ 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 cm$^{-1}$ is the bending of the top and bottom CaCl$_3$ fragments. The vibration modes $\omega_{13}$ ($E$) = 282 cm$^{-1}$, and $\omega_{14}$ ($E'$) = 264 cm$^{-1}$ correspond to the stretching vibrations of the attached CaCl$_2$ molecules and bipyramidal Ca$_3$Cl$_5^+$ moiety; these modes are similar to the vibrations 297 cm$^{-1}$ and 263 cm$^{-1}$ in the Ca$_4$Cl$_7^+$ ion.
Fig. 7. Equilibrium geometrical structure of the Ca$_4$Cl$_7^+$, C$_{2v}$ symmetry: (a) top view; (b) side view

Table 6. Properties of the undecaatomic Ca$_4$Cl$_7^+$ ion of C$_{2v}$ symmetry

| Property | DFT B1 | MP2 B1 |
|----------|--------|--------|
| $R_{e1}$(Ca$_v$–Cl$_h$) | 2.870 | 2.867 |
| $R_{e2}$(Ca$_v$–Cl$_h$) | 2.944 | 2.945 |
| $R_{e3}$(Ca$_v$–Cl) | 2.738 | 2.741 |
| $R_{e4}$(Ca–Cl) | 2.681 | 2.685 |
| $R_{e5}$(Ca–Cl$_h$) | 2.888 | 2.887 |
| $R_{e6}$(Ca–Cl$_h$) | 2.778 | 2.785 |
| $\alpha_e$(Cl$_h$–Ca$_v$–Cl$_h$) | 72.6 | 72.9 |
| $\alpha'_e$(Cl$_h$–Ca$_v$–Cl$_h$) | 76.4 | 73.5 |
| $\beta_e$(Cl–Ca$_v$–Cl) | 118.1 | 117.5 |
| $\gamma_e$(Cl–Ca–Cl) | 156.5 | 155.8 |
| $\varepsilon$ | 5932.21088 | 5925.86678 |
| $\mu_e$ | 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 |

* For Ca$_4$Cl$_7^+$ (C$_{2v}$) the vibrational representation is $\Gamma^* = 9A_1 + 5A_2 + 7B_1 + 6B_2$
Fig. 8A. The theoretical IR spectrum of the undecaatomic \( \text{Ca}_4\text{Cl}_7^+ \) ion (\( C_{2v} \))

(a) (b)

Fig. 8. Equilibrium geometrical structure of the \( \text{Ca}_5\text{Cl}_9^+ \) of \( D_{3h} \) symmetry: (a) top view (b) side view

Table 7. Properties of the tetradecanatomic \( \text{Ca}_5\text{Cl}_9^+ \) 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) |
| \( \alpha_4(\text{Ca}_h−\text{Cl}_h−\text{Cl}_h) \) | 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) | \( \omega_{10} (A'') \) |        |

* For \( \text{Ca}_5\text{Cl}_9^+ (D_{3h}) \) the vibrational representation is \( \Gamma = 8A'^+ + 4A'^+ + 6E' + 6E'' \)
4. CONCLUSION

The cluster ions \( \text{CaCl}^+, \text{CaCl}_2^-, \text{Ca}_2\text{Cl}_5^+, \text{Ca}_3\text{Cl}_5^+, \) and \( \text{Ca}_4\text{Cl}_7^+ \) have been detected earlier in the equilibrium vapour by high temperature mass spectrometry technique. The formation of the heavier cluster \( \text{Ca}_5\text{Cl}_9^+ \) 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 \( \text{CaCl}_2 \) molecule to \( \text{CaCl}^+ \) ion. Alternative configurations were considered but no isomers revealed. The equilibrium geometrical structures of the ions \( \text{Ca}_2\text{Cl}_3^+, \text{Ca}_3\text{Cl}_5^+, \) and \( \text{Ca}_4\text{Cl}_7^+ \) confirmed to be compact and rigid of a perfect shape and high symmetry. The equilibrium structure of the ion \( \text{Ca}_5\text{Cl}_9^+ \) is of lower symmetry, and therefore lower stability of the ion regarding dissociation with \( \text{CaCl}_2 \) molecule elimination may be expected.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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