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The structures, binding energies and vibrational frequencies of Ca_3 and Ca_4 – An application of the CCSD(T) method*

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Summary. The Ca_3 and Ca_4 metallic clusters have been investigated using state-of-the-art *ab initio* quantum mechanical methods. Large atomic natural orbital basis sets have been used in conjunction with the singles and doubles coupled-cluster (CCSD) method, a coupled-cluster method that includes a perturbational estimate of connected triple excitations, denoted CCSD(T), and the multireference configuration interaction (MRCI) method. The equilibrium geometries, binding energies and harmonic vibrational frequencies have been determined with each of the methods so that the accuracy of the coupled-cluster methods may be assessed. Since the CCSD(T) method reproduces the MRCI results very well, cubic and quartic force fields of Ca_3 and Ca_4 have been determined using this approach and used to evaluate the fundamental vibrational frequencies. The infrared intensities of both the e' mode of Ca_3 and the t_2 mode of Ca_4 are found to be small. The results obtained in this study are compared and contrasted with those from our earlier studies on small Be and Mg clusters.

Key words: Ca_3/Ca_4 metallic clusters – CCSD(T) method – Vibrational frequencies

1. Introduction

There has been considerable recent interest in the properties of small clusters (see for example [1–10]), motivated principally by two issues. The first is the question of convergence of cluster properties towards the bulk values. Of course some properties will approach the bulk value more quickly than others as the cluster size is increased. The second issue is interaction between theory and experiment. The study of small clusters has progressed very rapidly since accurate experimental studies may be used to evaluate the predictive reliability of different theoret-

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* Dedicated to Prof. Klaus Ruedenberg on the occasion of his 70th birthday

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*** *Mailing address*: NASA Ames Research Center, Moffett Field, CA, 94035, USA ical methods, and then accurate theoretical studies may be used to evaluate or aid in the design of new experimental techniques.

Our studies of small clusters [11, 12] have focused on computing the structures, binding energies, vibrational frequencies, and infrared intensities of the trimers and tetramers of the alkaline-earth elements beryllium and magnesium using elaborate treatments of electron correlation. We have also examined [13] the equilibrium structures and binding energies of the pentamers, Be_5 and Mg_5. In the present study we extend our investigations to include Ca_3 and Ca_4. There are three previous studies [14, 15, 16] of Ca_4 (and none of Ca_3) that have incorporated electron correlation effects. In two of these Ca_4 studies [14, 15] a total binding energy of 18.3 kcal/mol, relative to four Ca atoms, was obtained at the single-reference single and double excitation configuration interaction (CISD) level of theory, including Davidson's correction [17] for higher excitations. In the other [16], a binding energy of 13.9 kcal/mol was obtained using a multireference CI approach (based on SCF orbitals). Based on our previous studies of the Be and Mg clusters, it is likely that even the higher value is a substantial underestimate of the true binding energy.

Another important component of our earlier studies [11–13, 18] is the comparison of geometries and binding energies obtained with various electron correlation methods. The $s-p$ near-degeneracy effects in the alkaline-earth valence shell are very large, and strongly influence the binding in the small clusters. It is not only essential to describe these non-dynamical effects accurately, however, but also to account properly for dynamical correlation in order to obtain reliable binding energies for these systems. Hence the most desirable treatment might appear to be a full valence complete-active-space SCF (CASSCF) calculation followed by a multireference configuration-interaction (MRCI) calculation. This is indeed an excellent level of treatment, but unfortunately it becomes very expensive to apply in large basis sets and at many geometries.

In our studies of the lighter alkaline-earth clusters, we have made extensive use of the single and double excitation coupled-cluster (CCSD) approach corrected with a perturbational estimate of connected triple excitations (CCSD(T)) [19]. The CCSD(T) method performs very well in comparison with MRCI results for the lighter alkaline-earth clusters, and appears to treat both the non-dynamical and dynamical correlation effects in these systems accurately. We have also established the reliability of the CCSD(T) method by full CI comparisons on Be_3 [20]. For comparison purposes, we have again used the CCSD, CCSD(T) and MRCI methods in examining the potential energy surfaces of Ca_3 and Ca_4.

In the next section we describe the computational methods employed in this study and in the following section our results are presented and discussed. A comparison of our new results for the Ca clusters and our previous results for the Be and Mg clusters is also given. The final section contains our conclusions.

2. Computational methods

Two atomic natural orbital [21] (ANO) basis sets have been used in this study. The ($22s$ $17p$) primitive basis set is that of Partridge [22] and was augmented with a ($4d$ $3f$) even tempered polarization set defined by $\alpha = 2.5^n\alpha_0$ for $n = 0, \ldots, k$. The α_0 values for the d and f functions are 0.0232 and 0.0440, respectively. The smallest basis set consists of $5s$, $4p$ and $1d$ ANOs and will be denoted [5s 4p 1d]. The larger basis consists of 6s, 5p, 2d and 1f ANOs and will be denoted [6s 5p 2d 1f]. The ANO contraction coefficients were obtained by averaging the natural orbitals from CISD calculations on the lowest ^1S and ^1P states of atomic Ca. Only the pure spherical harmonic components of the *d* and *f* functions have been used.

As discussed in the Introduction, the CCSD, CCSD(T) and MRCI methods have been used to treat electron correlation. In all cases, only the Ca 4s electrons have been included in the correlation procedure. The coupled-cluster wave functions are based on self-consistent field (SCF) molecular orbitals while the MRCI wave functions are based on CASSCF molecular orbitals. All valence electrons were allowed variable occupancy in all valence orbitals in the CASSCF calculations (i.e., the Ca 4s and 4p-like molecular orbitals). References for the MRCI wave functions were selected using a 0.05 threshold – that is, all occupations having a component spin-coupling with a coefficient of 0.05 or larger in the CASSCF wave function were used as references in the MRCI procedure.

In analogy with small Be and Mg clusters, the equilibrium geometries of Ca_3 and Ca_4 were constrained to have D_{3h} and T_d symmetry, respectively. That is, the equilibrium structure of Ca_3 is an equilateral triangle whereas that of Ca_4 is a tetrahedron. Harmonic frequency analyses demonstrate explicitly that these geometries are indeed minima on the Ca_3 and Ca_4 potential energy surfaces. In addition, a linear structure for Ca_3 was optimized and found to be significantly higher in energy than the equilateral triangle. Hence it is expected that the equilateral triangle and tetrahedron are the global minima on the Ca_3 and Ca_4 potential energy surfaces, respectively.

The quadratic, cubic and quartic force constants of Ca_3 and Ca_4 have been determined numerically and are given in symmetry internal coordinates. The symmetry internal coordinate definitions are:

Ca_3

$$S_1(a_1') = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3) \tag{1}$$

$$S_{2a}(e') = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3) \tag{2}$$

$$S_{2b}(e') = \frac{1}{\sqrt{2}}(r_2 - r_3) \tag{3}$$

Ca_4

$$S_1(a_1) = \frac{1}{\sqrt{6}}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6) \tag{4}$$

$$S_{2a}(e) = \frac{1}{\sqrt{12}}(2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6) \tag{5}$$

$$S_{2b}(e) = \frac{1}{\sqrt{4}}(r_2 - r_3 + r_5 - r_6) \tag{6}$$

$$S_{3x}(t_2) = \frac{1}{\sqrt{2}}(r_2 - r_5) \tag{7}$$

$$S_{3y}(t_2) = \frac{1}{\sqrt{2}}(r_3 - r_6) \tag{8}$$

$$S_{3z}(t_2) = \frac{1}{\sqrt{2}}(r_1 - r_4). \tag{9}$$

For Ca_4, the numbering of bonds is such that if r_1 connects one pair of atoms, r_4 connects the other pair, and similarly for the pairs $\{r_2, r_5\}$ and $\{r_3, r_6\}$. According to convention [23], the a component of the doubly degenerate coordinates is defined such that it is symmetric with respect to a σ_v reflection plane, whereas the b component is antisymmetric. The x, y, and z components of the triply degenerate coordinate are also defined according to established convention [24].

The precision of the central difference numerical procedures used to obtain the force constants has been closely monitored: the uncertainty in the harmonic frequencies should be less than 0.1 cm^{-1} and in the fundamental frequencies less than 0.5 cm^{-1}. The anharmonic analyses have been performed with the SPECTRO program package [25] which uses second-order perturbation theory; Ca_3 has been treated as a symmetric top [23] and Ca_4 has been treated as a spherical top [26]. The coupled-cluster calculations were performed with the TITAN set of programs [27] interfaced to the MOLECULE-SWEDEN suite of programs [28]. The MRCI calculations were performed with MOLECULE-SWEDEN.

3. Results and discussion

3.1. Equilibrium structures and binding energies

Table 1 contains the equilibrium bond distances, rotational constants and dissociation energies (atomization energies) of Ca_3 and Ca_4 computed in this study. For Ca_3 the CCSD level of theory substantially underestimates the D_e value (i.e., 5.7 kcal/mol or 47% of the MRCI result) and therefore yields a bond length 0.22 a_0 longer than the MRCI value. However, the CCSD(T) level of

Table 1. Total energies (E_h), bond lengths (a_0), rotational constants (MHz) and binding energies (kcal/mol) for Ca_3 and Ca_4

		Basis	E^a	r_e	A	B	D_e	D_0
Ca_3	CCSD	[6*s* 5*p* 2*d* 1*f*]	0.370728	8.097	1378	689	6.4	6.1
	CCSD(T)	[6*s* 5*p* 2*d* 1*f*]	0.378316	7.884[b]	1453	726	11.2	10.8
	MRCI	[6*s* 5*p* 2*d* 1*f*]	0.379234	7.874	1457	728	12.1	11.7
Ca_4	CCSD	[5*s* 4*p* 1*d*]	0.168123	7.935	717		14.3	13.6
	CCSD(T)	[5*s* 4*p* 1*d*]	0.180604	7.806	741		22.2	21.4
	MRCI	[5*s* 4*p* 1*d*]	0.179059	7.824	738		22.4	21.7
	CCSD	[6*s* 5*p* 2*d* 1*f*]	0.180579	7.694	763		20.9	20.1
	CCSD(T)	[6*s* 5*p* 2*d* 1*f*]	0.197496	7.591[c]	784		31.5	30.6

[a] The energy for Ca_3 is reported as $-(E + 2030)$ and for Ca_4 as $-(E + 2707)$

[b] Vibrationally averaged bond lengths: $r_g = 7.917\ a_0$ and $r_\alpha = 7.915\ a_0$

[c] Vibrationally averaged bond lengths: $r_g = 7.615\ a_0$ and $r_\alpha = 7.613\ a_0$

theory exhibits a significant improvement over the CCSD results: D_e is only 0.9 kcal/mol less than the MRCI result and the equilibrium bond distance differs from the MRCI value by only 0.01 a_0. A similar situation is found with Ca_4 – the CCSD level of theory substantially underestimates the binding energy and gives an equilibrium bond distance 0.11 a_0 too long. However, as was found for the Be and Mg clusters [11, 12], the CCSD level of theory performs better for Ca_4 than it does for Ca_3. The CCSD(T) results for Ca_4 (using the smaller ANO basis set) are in very good agreement with the respective MRCI quantities. The CCSD(T) D_e is only 0.2 kcal/mol less than the MRCI value and the CCSD(T) r_e is actually 0.02 a_0 shorter than the MRCI r_e. As with our earlier studies [11, 12] of small Be and Mg clusters, it thus appears that the CCSD(T) level of theory provides a very good description of electron correlation effects in small Ca clusters.

It is interesting to note that comparison of the equilibrium bond distances obtained with the CCSD, CCSD(T), and MRCI methods suggests that the bonding in small Ca clusters is intermediate between the bonding in small Be and small Mg clusters, as would be expected based on the bulk binding energies (77, 35, and 42 kcal/mol for Be, Mg, and Ca, respectively) [29]. For Be_3, where *sp* hybridization is known to play an important role in the binding, the CCSD level of theory yields a reasonable equilibrium bond distance when compared to MRCI or CCSD(T). However, for Mg_3, where the binding is more dominated by dispersion, the CCSD level of theory gives a bond distance that is significantly too long (0.55 a_0). The discrepancy in the CCSD bond length for Ca_3 is between that found for Be_3 and Mg_3, but is much closer to the discrepancy obtained for Be_3 than that found for Mg_3. It therefore seems that *sp* hybridization is an important component of the bonding in Ca_3, though not as important as it is in the bonding of Be_3.

For Ca_4, only the CCSD and CCSD(T) levels of theory could be used in conjunction with the larger ANO basis set since the MRCI procedure would have been prohibitively expensive. Using the [6*s* 5*p* 2*d* 1*f*] ANO basis set, the CCSD(T) equilibrium bond distance for Ca_4 is 0.29 a_0 shorter than the analogous Ca_3 value indicating the increased importance of *sp* hybridization in the bonding as the cluster size becomes larger. The best D_e values for Ca_3 and Ca_4 obtained in this work are 12.1 kcal/mol and 31.5 kcal/mol, respectively. As expected, our best computed D_e for Ca_4 is substantially larger than the previously best computed value [14]. Based on the fact that the separated-atom limit is described better than the molecule, the D_e values for Ca_3 and Ca_4 are probably underestimated somewhat. We say "probably" because it is not certain whether the effects of core-correlation will increase or decrease the D_e values. However, based on a recent study of Ca_2 by Dyall and McLean [30], it is likely that the effects of core-correlation will not affect the D_e values by more than 1–2 kcal/mol.

3.2. *Vibrational frequencies of* Ca_3

The quadratic force constants and harmonic frequencies of Ca_3 obtained at the CCSD, CCSD(T), and MRCI levels of theory are presented in Table 2. The [6*s* 5*p* 2*d* 1*f*] ANO basis set was used with all of these methods. In view of the underestimation of the bond strength at the CCSD level, it is not surprising that the CCSD quadratic force constants and harmonic frequencies are noticeably

Table 2. Symmetry internal coordinate force constants (aJ/Å^2) and harmonic frequencies (cm^{-1}) for Ca_3

	F_{11}	F_{22}	$\omega_1(a_1')$	$\omega_2(e')$
CCSD	0.04415	0.08141	75	72
CCSD(T)	0.06952	0.10835	94	83
MRCI	0.07126	0.11460	95	85

smaller than the analogous MRCI values. Conversely, the CCSD(T) quadratic force constants and harmonic frequencies are in excellent agreement with the MRCI quantities, being only 1 cm^{-1} and 2 cm^{-1} smaller for the a_1' and e' modes, respectively. The best computed harmonic frequencies of Ca_3 obtained in this work are 95 cm^{-1} and 85 cm^{-1} for the a_1' and e' modes, respectively. These values should be reasonably reliable and are probably low rather than high, assuming that the binding energy is still somewhat underestimated. The harmonic frequencies of Ca_3 are small not only because the bonding in Ca_3 is relatively weak, but also because of the large mass of the Ca atom and the $1/\sqrt{m}$ dependence of the harmonic frequency, where m is the reduced mass of the system.

We have computed cubic and quartic force constants using the CCSD(T) method, since the CCSD(T) and MRCI harmonic frequencies are in excellent agreement and the former approach is significantly cheaper. The complete set of cubic and quartic force constants and the resulting anharmonic constants are presented in Table 3. Table 4 contains the fundamental vibrational frequencies of Ca_3 determined via second-order perturbation theory. In addition, Table 4 presents the infrared (IR) intensity of the e' vibration determined using the double harmonic approximation.

Table 3. Non-zero cubic (aJ/Å^3) and quartic (aJ/Å^4) force constants and the anharmonic constants (cm^{-1}) for Ca_3

F_{111}	−0.133
$F_{12a2a} = F_{12b2b}$	−0.152
$F_{2a2a2a} = -F_{2a2b2b}$	−0.105
F_{1111}	0.156
$F_{112a2a} = F_{112b2b}$	0.163
$F_{12a2a2a} = -F_{12a2b2b}$	0.116
$F_{2a2a2a2a} = F_{2b2b2b2b} = 3F_{2a2a2b2b}$	0.239
Anharmonic constants	
x_{11}	−0.60
x_{21}	−1.38
x_{22}	−0.41
g_{22}	0.18

Table 4. Comparison of the CCSD(T) harmonic and fundamental frequencies of Ca_3 (cm^{-1}). Infrared intensities (km/mol) are also included

Mode	ω	ν	$\omega - \nu$	I
a_1'	94	92	2	0
e'	83	81	2	0.4

The absolute anharmonic contribution to the vibrational frequencies is small, only 2 cm^{-1} for both vibrations, and the percentage effect is about half that observed previously for the Mg clusters. Combining the MRCI harmonic frequencies with the anharmonic correction obtained with the CCSD(T) method gives 93 cm^{-1} and 83 cm^{-1} as our best estimates for the fundamental vibrational frequencies of the a_1' and e' modes, respectively. Because the IR intensity of the e' mode is so small, the best prospect for determining the vibrational frequencies experimentally is likely to be an indirect technique such as negative ion photoelectron spectroscopy.

3.3. *Vibrational frequencies of* Ca_4

The quadratic force constants and harmonic frequencies of Ca_4, determined at the CCSD, CCSD(T), and MRCI levels of theory, are presented in Table 5. A noteworthy point is that the CCSD harmonic frequencies are in better agreement with the MRCI values than was found for Ca_3. This is especially true for ω_2 and ω_3 where the differences are only 4 cm^{-1} and 8 cm^{-1}, respectively. This observation supports our earlier analysis regarding the increased importance of *sp* hybridization, and consequently covalent bonding, in Ca_4 relative to Ca_3. The CCSD(T) quadratic force constants and harmonic frequencies are in excellent agreement with the respective MRCI quantities. Indeed, ω_1 and ω_2 only differ by 1 cm^{-1} and ω_3 differs by less than this. These comparisons suggest that the CCSD(T) level of theory is closely approaching the n-particle limit for Ca_4.

The CCSD and CCSD(T) harmonic frequencies obtained with the larger [6*s* 5*p* 2*d* 1*f*] ANO basis set demonstrate the importance of using large one-particle basis sets in order to obtain highly accurate harmonic frequencies. The difference between the CCSD(T) harmonic frequencies in the two basis sets used is larger than the differences due to correlation treatment among the small basis results. For both Ca_3 and Ca_4 we expect core-correlation will have only a small effect on the vibrational frequencies, but investigation of this small effect is beyond the scope of the present study. As with Ca_3, it is expected that the CCSD(T)/[6*s* 5*p* 2*d* 1*f*] quadratic force constants and harmonic frequencies for Ca_4 should be very reliable.

Table 6 contains the complete cubic and quartic force field of Ca_4 obtained at the CCSD(T) level of theory with the larger ANO basis set. The resulting anharmonic constants are given in Table 7, while the fundamental vibrational

Table 5. Symmetry internal coordinate quadratic force constants (aJ/Å^2) and harmonic frequencies (cm^{-1}) for Ca_4

	Basis	F_{11}	F_{22}	F_{33}	$\omega_1(a_1)$	$\omega_2(e)$	$\omega_3(t_2)$
CCSD	[5*s* 4*p* 1*d*]	0.05350	0.12546	0.08688	95	73	86
CCSD(T)	[5*s* 4*p* 1*d*]	0.07166	0.14253	0.10439	110	78	94
MRCI	[5*s* 4*p* 1*d*]	0.06960	0.14091	0.10397	109	77	94
CCSD	[6*s* 5*p* 2*d* 1*f*]	0.07463	0.15725	0.11282	113	82	98
CCSD(T)	[6*s* 5*p* 2*d* 1*f*]	0.09446	0.17250	0.13062	127	86	105

Table 6. Non-zero cubic (aJ/Å^3) and quartic (aJ/Å^4) force constants for Ca_4

F_{111}	−0.110
$F_{12a2a} = F_{12b2b}$	−0.140
$F_{13x3x} = F_{13y3y} = F_{13z3z}$	−0.126
$F_{2a2a2a} = -F_{2a2b2b}$	−0.074
$F_{2a3z3z} = -2F_{2a3x3x} = -2F_{2a3y3y} = \frac{2}{\sqrt{3}}F_{2b3x3x} = \frac{-2}{\sqrt{3}}F_{2b3y3y}$	−0.190
F_{3x3y3z}	−0.013
F_{1111}	0.077
$F_{112a2a} = F_{112b2b}$	0.091
$F_{113x3x} = F_{113y3y} = F_{113z3z}$	0.076
$F_{12a2a2a} = -F_{12a2b2b}$	0.058
$F_{12a3z3z} = -2F_{12a3x3x} = -2F_{12a3y3y} = \frac{2}{\sqrt{3}}F_{12b3x3x} = \frac{-2}{\sqrt{3}}F_{12b3y3y}$	0.119
$F_{13x3y3z}$	−0.001
$F_{2a2a2a2a} = F_{2b2b2b2b} = 3F_{2a2a2b2b}$	0.162
$F_{2a2a3z3z}$	0.176
$F_{2b2b3z3z}$	0.044
$^aF_{2a2a3y3y} = F_{2a2a3x3x} = \frac{1}{4}(F_{2a2a3z3z} + 3F_{2b2b3z3z})$	0.077
$^aF_{2b2b3y3y} = F_{2b2b3x3x} = \frac{1}{4}(3F_{2a2a3z3z} + F_{2b2b3z3z})$	0.143
$^aF_{2a2b3y3y} = -F_{2a2b3x3x} = \frac{\sqrt{3}}{4}(F_{2a2a3z3z} - F_{2b2b3z3z})$	0.057
$F_{3x3x3x3x} = F_{3y3y3y3y} = F_{3z3z3z3z}$	0.262
$F_{3x3x3y3y} = F_{3x3x3z3z} = F_{3y3y3z3z}$	0.043

[a] Dependent force constants related to $F_{2a2a3z3z}$ and $F_{2b2b3z3z}$

Table 7. Anharmonic constants (cm^{-1}) for Ca_4

Anharmonic constants	
x_{11}	−0.31
x_{21}	−0.52
x_{22}	−0.13
x_{31}	−0.83
x_{32}	−0.35
x_{33}	−0.18
g_{22}	0.09
g_{33}	0.03
t_{23}	−0.05
t_{33}	−0.03

Table 8. Comparison of the CCSD(T) harmonic and fundamental frequencies of Ca_4 (cm^{-1}). Infrared intensities (km/mol) are also included

Mode	ω	ν	$\omega - \nu$	I
a_1	127	124	3	0
e	86	85	1	0
t_2	105	104	1	2.1

frequencies and IR intensities of Ca_4 are presented in Table 8. As with Ca_3, the absolute anharmonic corrections for the vibrational modes of Ca_4 are relatively small at only 3 cm^{-1}, 1 cm^{-1}, and 1 cm^{-1} for ω_1, ω_2, and ω_3, respectively. The percentage effect on the fundamental frequencies is also similar to that found for Ca_3. The IR intensity of the t_2 vibration is 2.1 km/mol, which is substantially larger than the IR intensity of the e' vibration in Ca_3, but again the best method to obtain fundamental frequencies from experiment may be an indirect approach.

3.4. *Summary of* CCSD(T) *results for small* Be, Mg, *and* Ca *clusters*

A summary of the equilibrium structures, vibrational frequencies, infrared intensities and binding energies for the alkaline-earth trimers is presented in Table 9 and for the tetramers in Table 10. The beryllium and magnesium cluster results are taken from our previous studies [11, 12]. In all cases, the results are those obtained with the largest ANO basis set used in the particular investigation. For the trimers, Table 9 contains the MRCI equilibrium bond distance, harmonic frequencies and dissociation energy. The fundamental frequencies were obtained by adding the CCSD(T) anharmonicity to the MRCI harmonic frequencies. The IR intensities were determined with the CCSD(T) method. For the tetramers, all of the results were obtained at the CCSD(T) level of theory since it was not possible to use the MRCI method in conjunction with the larger ANO basis sets for the tetramers. Thus the values summarized in Tables 9 and 10 represent the best computed quantities to date for the alkaline-earth trimers and tetramers.

Examination of the binding energies in Table 9 indicates the expected trend based on bulk binding energies – that is the binding energies decrease in the order $Be_3 > Ca_3 > Mg_3$. The vibrational frequencies, on the other hand, decrease in the order $Be_3 > Mg_3 > Ca_3$, but this is determined in large part by mass effects, since the symmetry internal coordinate quadratic force constants for Mg_3 are smaller [12] than those for Ca_3. The IR intensity of the e' mode is small for all of the alkaline-earth trimers.

Table 9. Summary of results for the alkaline earth trimers[a]

	r_e	$\omega_1(a_1')$	$\omega_2(e')$	ν_1	ν_2	D_e
Be_3	4.200	490	427(0.5)	469	410	22.5
Mg_3	6.373	110	115(0.2)	101	109	6.3
Ca_3	7.874	95	85(0.4)	93	83	12.1

[a] Units are a_0 for r_e, cm^{-1} for the harmonic and fundamental frequencies, and kcal/mol for D_e. The value in parentheses is the IR intensity in km/mol. The Be_3 results are from [11] and the Mg_3 results are from [12]. See text for details of correlation methods used

Table 10. Summary of CCSD(T) results for the alkaline earth tetramers[a]

	r_e	$\omega_1(a_1)$	$\omega_2(e)$	$\omega_3(t_2)$	ν_1	ν_2	ν_3	D_e
Be_4	3.921	663	469	571(29.7)	639	455	682	79.5
Mg_4	5.877	192	147	171(2.4)	184	143	167	23.9
Ca_4	7.591	127	86	105(2.1)	124	85	104	31.5

[a] Units are a_0 for r_e, cm^{-1} for the harmonic and fundamental frequencies, and kcal/mol for D_e. The value in parentheses is the IR intensity in km/mol. The Be_4 results are from [11] and the Mg_4 results are from [12]

Comparison of the D_e values of the tetramers shows the same trend observed for the trimers, although the ratios are somewhat different. The binding energy of Be_4 is significantly larger than that of Be_3, though the Be_4 equilibrium bond distance is only 0.28 a_0 shorter than the Be_3 value. The ratio $D_e(M_4)/D_e(M_3)$ is largest for M = Mg and it is therefore not surprising that Mg_4 exhibits the largest reduction in bond length (0.50 a_0) relative to the trimer. The reduction in the Ca_4 bond length (relative to the trimer) is about the same as that observed for Be even though the ratio $D_e(M_4)/D_e(M_3)$ is significantly larger for M = Be than for M = Ca. This last observation is probably due to the fact that the valence orbitals of Ca are larger than those of Be.

The harmonic frequencies of the tetramers exhibit the same trend as observed for the trimers. Again, the Mg_4 vibrational frequencies are higher than the analogous Ca_4 values because of the mass effect. The fundamental frequency ν_3 for Be_4 has a large *positive* anharmonic correction that is not observed in either Mg_4 or Ca_4. This Be_4 phenomenon was explained in some detail previously [11], and relies on a symmetry argument applicable to tetrahedral X_4 species. Its apparent inapplicability to Mg_4 and Ca_4 is probably due to several factors, including the much weaker bonds present in Mg_4 and Ca_4 relative to Be_4. The IR intensities of the tetramer t_2 vibrations are much larger than those calculated for the trimers. Nevertheless, the Mg_4 and Ca_4 intensities remain very small and it is likely that the best prospect for experimental determination of these frequencies will be an indirect method like negative ion photodetachment. On the other hand, the IR intensity of the t_2 mode of Be_4 is certainly large enough to allow direct experimental observation provided that an experiment can be designed which will produce enough Be_4.

4. Conclusions

The CCSD, CCSD(T), and MRCI electron correlation methods have been used to investigate the equilibrium structures, vibrational frequencies and binding energies of the Ca_3 and Ca_4 metallic clusters. In agreement with our earlier studies of the analogous Be and Mg clusters, it is found that the CCSD(T) method reproduces the MRCI r_e, harmonic frequencies and D_e values very well. The agreement between these methods is somewhat better for Ca_4, but is still very good for Ca_3. Complete cubic and quartic force fields of Ca_3 and Ca_4 have been determined with the CCSD(T) method in conjunction with a large ANO basis set and have been used to evaluate the anharmonic corrections needed to compute the funadmental frequencies. The anharmonic corrections have been determined via second-order perturbation theory. The absolute value of the anharmonic corrections is relatively small, although as a percentage relative to the fundamental frequencies they are similar to those observed previously for the Mg clusters. In spite of the fact that Ca is larger and more polarizable than Mg, and that Ca clusters are more strongly bound than Mg clusters, the IR intensities of the e' mode of Ca_3 and of the t_2 mode of Ca_4 are small and similar to the analogous Mg quantities. It is unlikely that direct observation of these fundamentals will be possible.

The MRCI and CCSD(T) equilibrium structures, vibrational frequencies and binding energies of the alkali metal (Be, Mg, and Ca) trimers and tetramers have been summarized. The binding energies of the trimers and tetramers follow the bulk metal binding energies although the ratios of the small cluster D_e values do not agree with the bulk metal ratios. The vibrational frequencies follow a different trend as the Mg_n ($n = 3, 4$) frequencies are larger than the respective Ca values, but this is due to the larger mass of the Ca atom, since the symmetry internal coordinate force constants (which are independent of mass) for the Ca trimer and tetramer are larger than the respective Mg quantities.

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