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Magnesium- and calcium-containing molecular dications: a high-level theoretical study

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Abstract

High-level ab initio quantum chemical calculations, using the GAUSSIAN-2 (G2), G2(MP2), and G2(QCI) procedures, are reported for the species MX^{2+} ($M = Mg$ and Ca; $X = NH_3$, H_2O, HF, PH_3, H_2S, HCl, CO, and N_2). In most instances, these molecular dications are predicted to be thermodynamically stable with respect to the lowest energy dissociation products. For $M(CO)^{2+}$, the two linear geometries MCO^{2+} and MOC^{2+} are both found to represent strongly bound equilibrium structures, with the MCO^{2+} isomer lying lower in energy. It is hoped that the present thermochemical data may aid in future experimental investigations of metal-containing dications. (Int J Mass Spectrom 192 (1999) 173–183) © 1999 Elsevier Science B.V.

Keywords: Magnesium; Calcium; Dications; Ab initio

1. Introduction

Gas-phase dications [1,2], and their reactions with neutral molecules [3], have received considerably less attention than has been accorded their monocationic counterparts. This is an obvious consequence of the somewhat greater difficulties inherent in the study of doubly charged, versus singly charged, species. Molecular dications are subject to sizeable electrostatic strain effects arising from intramolecular coulombic repulsion, and their formation necessitates more energetic ionization processes (e.g. high energy electron impact ionization) than are required to form monocations. There is thus a common conception that gas-phase dications are a rather “frail” species. Nevertheless, there currently exists a sizeable quantity of experimental data on the reactions of atomic (e.g. Ar^{2+} [4]), small molecular (e.g. CCl_3^{2+} [5]), and larger molecular (e.g. C_{60}^{2+} [6]) dications with a variety of neutral molecules.

One of the pioneering studies in dication/molecule chemistry involved the reactions of Mg^{2+}, Ca^{2+}, or Ba^{2+} (generated by electron impact double ionization of the relevant, vaporized, alkaline earth) with a series of neutrals, including Ar, CO, H_2O, and N_2, in a flowing afterglow apparatus by using helium as a buffer gas at a temperature of 300 K [7]. This study, which also yielded information on the reaction chemistry of the monocationic metal atoms with the same neutrals, revealed two important and perhaps unexpected general trends. First, partial charge transfer

$$M^{2+} + X \rightarrow M^{+} + X^{+} \qquad (1)$$

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was often not observed, even when significantly exothermic; and second, the termolecular rate coefficients for association

$$M^{2+} + X + He \rightarrow MX^{2+} + He^{*} \quad (2)$$

typically exceeded the association rate coefficients for the same neutral X with the analogous monocation M^{+} by a factor of several hundred. Theoretical models [8,9] have sought to rationalize the dependence of the barriers for the partial-charge–transfer reactions on reaction exothermicity. Such models involve an avoided crossing between the attractive potential of $M^{2+} + X$ and the repulsive curve represented by $M^{+} + X^{+}$, and the agreement between theory and experiment (for simple reactants) is often rather good.

Although Spears and Fehsenfeld's flowing afterglow study [7] was conducted a quarter-century ago, several of the molecular dications which they reported have received very little subsequent scrutiny. Advances in techniques such as electrospray ionization [10] have permitted the laboratory generation of significantly hydrated metal dications [11,12], but the primary adducts such as $CaOH_2^{2+}$ appear not to have been subjected to further laboratory study. Theoretical attention has also been focused almost exclusively—if somewhat understandably—upon the aquo complexes $M(H_2O)_n^{2+}$ [13–23], although some investigation of the complexes of Mg^{2+} or Ca^{2+} with NH_3, HF, PH_3, H_2S, HCl, N_2, CO, and Ar has also been reported [16,20,22,24–28]. In the present work, we describe calculations, using modified versions of the GAUSSIAN-2 (G2) [29] and G2(QCI) [30] techniques, on the monoadducts of Mg^{2+} and Ca^{2+} with a series of ligands, including most of those contained in Spears and Fehsenfelds's original study [7].

2. Theoretical methods

Total energies for the molecular dications MX^{2+} were obtained using modified versions of the G2 technique [29,31], as follows. Geometries were optimized at the QCISD/6-311G** level of theory, with the correlation space for these calculations including Mg 2*s* and 2*p*, or Ca 3*s* and 3*p*, orbitals in addition to the standard "valence" orbitals for all atoms. The same correlation space was implemented for the single-point energy calculations [MP4/6-311G**, MP4/6-311+G**, MP4/6-311G(2*df*,*p*), QCISD(T)/6-311G**, and MP2/6-311+G(3*df*,2*p*)] required for the G2 energy. Such a correlation space is standard for G2 calculations on Ca-containing species [31], but not for Mg-containing structures although a recent study [32] has indicated that inclusion of Na 2*s* and 2*p* orbitals amongst those correlated leads to substantially more accurate G2-like total energies for some sodium-containing ions. Similarly, the use of QCISD/6-311G** geometries (rather than MP2/6-31G* as employed in standard G2) was felt necessary so as to minimise any difficulties arising from poor-quality geometries, which have been identified [33] as problematic in the standard G2 treatment of small molecular dications. In a recent study concerning the isomeric dications $CaNCH^{2+}$ and $CaCNH^{2+}$ [34], we have found good agreement between QCISD/6-31G*, QCISD/6-311G**, B3-LYP/6-31G*, and B3-LYP/6-311G** optimized geometries, whereas MP2/6-31G* and MP2/6-311G** are not in particularly good agreement with the QCISD or B3-LYP geometries, or with one another. Furthermore, G2(MP2) total energies and enthalpies of formation obtained using either MP2/6-31G* or MP2/6-311G** geometries for $CaCN^{2+}$ are higher—and therefore presumably describe points further from the true minimum of the potential energy well for this species—than analogous G2(MP2) calculations using QCISD, B3-LYP, or HF geometries [34]. Zero-point energy (ZPE) and higher-level corrections (HLC) used in the present work are identical to those of standard G2, except that for the purposes of determining the HLC the Mg 2*s* and 2*p* electrons are treated as valence electrons.

Analogous calculations, featuring similarly defined optimized geometries and correlation spaces, were also performed at the G2(MP2) [35] and G2(QCI) [30] levels. We note that G2(MP2) is computationally less expensive but slightly less reliable than standard G2, whereas G2(QCI) is more reliable than G2 because it avoids the additivity approximations of the standard G2 approach. All calculations reported

Table 1
Optimized geometries for $M(CO)^{2+}$ stationary points as a function of theoretical method[a]

		HF	MP2(full)		QCISD[b]		B3-LYP	
Species	Parameter	6-31G*	6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
$CaCO^{2+}$	r(Ca–C)	2.684	2.608	2.622	2.630	2.645	2.589	2.619
	r(C–O)	1.098	1.142	1.130	1.134	1.120	1.123	1.113
$Ca(CO)^{2+}$ TS	r(Ca–C)	2.840	2.816	2.873	2.807	2.851	2.755	2.812
	r(C–O)	1.112	1.156	1.144	1.141	1.137	1.141	1.131
	∠(CaCO)	86.87°	74.80°	72.22°	81.44°	77.38°	77.37°	76.53°
$CaOC^{2+}$	r(Ca–O)	2.349	2.362	2.386	2.358	2.374	2.308	2.338
	r(O–C)	1.140	1.169	1.158	1.169	1.157	1.163	1.154
$MgCO^{2+}$	r(Mg–C)	2.263	2.229	2.227	2.241	2.238	2.226	2.225
	r(C–O)	1.093	1.140	1.129	1.129	1.118	1.120	1.110
$Mg(CO)^{2+}$ TS	r(Mg–C)	2.398	2.449	2.472	2.415	2.428	2.405	2.422
	r(C–O)	1.115	1.161	1.150	1.154	1.142	1.145	1.136
	∠(MgCO)	82.56°	71.04°	69.01°	75.54°	73.88°	74.47°	73.13°
$MgOC^{2+}$	r(Mg–O)	1.970	2.036	2.028	2.017	2.011	1.988	2.001
	r(O–C)	1.149	1.177	1.166	1.177	1.166	1.171	1.162

[a] Bond lengths in angstroms, bond angles in degrees.

[b] The correlation spaces for these calculations exclude 1s orbitals for Mg, C, and O, and 1s, 2s, and 2p orbitals for Ca.

herein were obtained using the GAUSSIAN 94 programming suite [36].

3. Results and discussion

Optimized geometries for the MgX^{2+} and CaX^{2+} species, obtained at the QCISD/6-311G** level of theory, are detailed in Table 1 [$M(CO)^{2+}$ isomers] and Fig. 1 (other dications). Total energies for these species, using the modified G2, G2(MP2), and G2(QCI) methods described previously, are shown in Table 2. Also included in Table 2 are enthalpies of formation at 0 K ($\Delta H^{\circ}_{f,0}$), calculated in the normal manner [37], and metal dication affinities (MDAs). In the discussion that follows, we shall compare the present results with those reported previously by other researchers.

3.1. General comments

In an earlier study (which did not include the extended correlation spaces incorporated in our present calculations) [33], we demonstrated that the differences between G2, G2(MP2), and G2(QCI) enthalpies of formation for small molecular dications are often substantially larger than the corresponding differences between these values for neutral mole-

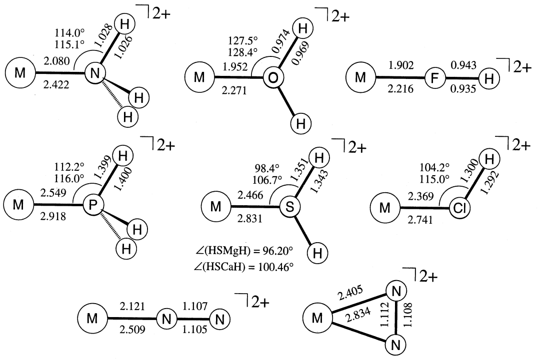

Fig. 1. Optimized geometries for MX^{2+} stationary points, obtained at the QCISD/6-311G** level of theory with correlation spaces as defined within the text. Interatomic distances, in angstroms, and bond angles in degrees, are shown for M = Mg (upper value) and Ca (lower value).

Table 2
G2, G2(MP2), and G2(QCI) total energies, enthalpies of formation, and metal dication affinities for MX^{2+} species

		G2[a]			G2(MP2)[a]			G2(QCI)[a]		
Species	ZPE[b]	E_0[c]	$\Delta H^\circ_{f,0}$[d]	MDA(X)[e]	E_0[c]	$\Delta H^\circ_{f,0}$[d]	MDA(X)[e]	E_0[c]	$\Delta H^\circ_{f,0}$[d]	MDA(X)[e]
Mg^{2+}		−198.962 03	2332.4		−198.961 96	2334.5		−198.963 76	2325.1	
$MgNH_3^{2+}$	36.984	−255.570 25	1901.6	392.8	−255.567 89	1905.3	390.6	−255.572 82	1893.7	393.0
$MgOH_2^{2+}$	23.340	−275.419 17	1763.8	328.3	−275.416 35	1764.3	326.5	−275.421 87	1756.7	329.6
$MgFH^{2+}$	9.204	−299.398 92	1827.4	227.5	−299.395 64	1827.8	226.9	−299.401 70	1820.4	229.1
$MgPH_3^{2+}$	26.495	−541.778 50	1987.9	360.7	−541.773 58	1991.3	360.6	−541.781 03	1979.8	359.7
$MgSH_2^{2+}$	17.700	−598.012 79	2000.0	315.1	−598.006 53	1997.4	316.3	−598.015 50	1994.0	314.1
$MgClH^{2+}$	8.020	−659.389 84	2008.5	230.1	−659.381 33	2006.7	230.4	−659.393 05	2002.7	229.1
$MgNN^{2+}$	7.411	−308.422 33	2159.9	173.4	−308.419 51	2160.4	174.3	−308.424 93	2153.7	173.6
$Mg(N_2)^{2+}$ TS	5.989	−308.390 61	2243.2	90.1	−308.387 47	2244.5	90.2	−308.393 29	2236.7	90.6
$MgCO^{2+}$	7.257	−312.219 04	2002.1	207.3	−312.216 52	2000.8	206.4	−312.221 90	1996.1	207.4
$Mg(CO)^{2+}$ TS	5.478	−312.176 68	2113.4	96.0	−312.174 69	2110.6	96.6	−312.179 77	2106.7	96.8
$MgOC^{2+}$	6.065	−312.205 12	2038.7	170.7	−312.203 22	2035.7	171.5	−312.208 16	2032.1	171.3
Ca^{2+}		−676.405 60	1906.5		−676.397 16	1911.1		−676.406 36	1905.6	
$CaNH_3^{2+}$	36.480	−732.961 14	1614.1	254.5	−732.950 98	1605.6	253.8	−732.962 89	1612.2	255.1
$CaOH_2^{2+}$	23.141	−752.822 29	1444.2	222.1	−752.811 66	1432.6	221.7	−752.824 05	1443.3	223.5
$CaFH^{2+}$	9.422	−776.815 57	1472.2	156.9	−776.804 25	1461.1	157.1	−776.817 26	1471.9	158.1
$CaPH_3^{2+}$	25.750	−1019.159 20	1727.1	195.7	−1019.145 74	1720.4	195.1	−1019.160 79	1725.3	194.7
$CaSH_2^{2+}$	17.032	−1075.402 64	1715.1	174.1	−1075.387 77	1702.6	174.6	−1075.404 53	1715.2	173.4
$CaClH^{2+}$	7.558	−1136.793 63	1687.2	125.6	−1136.776 77	1674.7	126.0	−1136.796 04	1687.2	125.1
$CaNN^{2+}$	6.972	−785.836 62	1810.9	96.5	−785.825 49	1813.8	97.6	−785.838 19	1811.2	96.6
$Ca(N_2)^{2+}$ TS	5.865	−785.815 81	1865.5	41.9	−785.804 44	1869.1	42.3	−785.817 59	1865.3	42.5
$CaCO^{2+}$	6.722	−789.627 80	1667.7	115.9	−789.616 96	1668.7	115.2	−789.629 56	1668.3	115.6
$Ca(CO)^{2+}$ TS	5.321	−789.600 15	1740.3	43.3	−789.589 81	1740.0	43.9	−789.602 17	1740.2	43.7
$CaOC^{2+}$	5.842	−789.620 87	1685.9	97.7	−789.610 84	1684.7	99.1	−789.622 89	1685.8	98.1

[a] In all instances, total energies reported here are for molecular geometries optimized at the QCISD/6-311G** level of theory [with the correlation space including 2*s* and 2*p* (Mg) or 3*s* and 3*p* (Ca) electrons as well as valence electrons for all atoms] rather than the standard MP2(full)/6-31G* level. This "relaxed-inner-valence" correlation space is also used for the single-point total-energy calculations appropriate to the G2, G2(MP2), or G2(QCI) methods.

[b] Zero-point vibrational energy in mHartrees (1 mHartree = 2.6255 kJ mol^{-1}), obtained at the HF/6-31G* level of theory (corrected by a factor of 0.8929).

[c] Total energy (in Hartrees), including ZPE, at the indicated level of theory.

[d] Enthalpy of formation (at 0 K), in kilojoules per mole, at the indicated level of theory.

[e] Metal dication affinity of the neutral ligand, in kilojoules per mole, at the indicated level of theory. This parameter is equivalent to the M^{2+}–X bond strength. As for the dicationic species, total energies for the ligands X refer to QCISD(fc)/6-311G** optimized geometries.

cules or singly charged ions. The concept that significant discrepancies should exist between such closely related and computationally intensive theoretical procedures is problematic, particularly because there are relatively few reliable experimental benchmarks to assess current theoretical thermochemical values for small molecular dications. It is hoped that the paucity of high-precision experimental data on molecular dications can soon be rectified.

Notwithstanding these concerns, there are good grounds for expecting that the values reported here for MgX^{2+} and CaX^{2+} are the most precise thermochemical data currently available for these species. First, the calculations are performed at levels of theory which are considered to be among the most accurate of widely accessible computational procedures. Second, the agreement between G2, G2(MP2), and G2(QCI) enthalpies of formation for our MgX^{2+} and CaX^{2+} dications (Table 2) is very encouraging. There are no instances where the additivity assumptions inherent in G2 and G2(MP2) [30] appear to be violated. The contrast in this regard between the present results and those of our earlier study [33] may arise from differences in the nature of the species investigated in these two studies. Our earlier investigation [33] included many open-shell species, or species prone to yield open-shell fragments upon dissociation, whereas all of the species of concern in the present work are closed-shell species formed (in principle) by the association of a closed-shell metal dication with a closed-shell ligand. Third, even the small differences that are seen here in our calculated enthalpies of formation at the G2, G2(MP2), and G2(QCI) levels of theory appear to be systematic and relate to the different enthalpies of formation of the atomic dications Mg^{2+} and Ca^{2+} at these levels. Thus, a comparison of the MDA of the various ligands (Table 2) reveals that agreement between G2, G2(MP2), and G2(QCI) for this parameter is significantly better than the agreement seen between enthalpies of formation. The close match between G2 and G2(QCI) MDA values (always better than ± 2 kJ mol^{-1}) is particularly encouraging.

Recent studies [31,38] have shown that quadratic configuration interaction calculations including single, double, and perturbative triple excitations [QCISD(T)] on CaO yield inappropriate total-energy values which lead to inaccurate enthalpies of formation at the G2 and G2(QCI) levels of theory. These failings can be very satisfactorily addressed by substitution of a coupled cluster calculation involving single, double, and perturbative triple excitations [CCSD(T)] for the corresponding QCISD(T) step in standard G2 or G2(QCI). In the present study, we have performed CCSD(T)/6-311G** calculations for a representative sample of the CaX^{2+} species surveyed here. The G2 and G2(MP2) total energies and MDA values obtained with the CCSD(T) calculations agree to within ± 1 kJ mol^{-1} of the corresponding values resulting from the use of QCISD(T)/6-311G** total energies. We conclude that the problems sometimes evident in QCISD(T) calculations on species containing third-row elements [38] do not appear to affect the G2 and G2(QCI) results reported here.

A comment on the use of MDA values in the present study is also warranted. In several instances, dissociation of MX^{2+} to $M^{2+} + X$ is not the lowest-energy fragmentation process, since I.E.(M^{+}) exceeds I.E.(X). This is the case for M = Mg for all X except HF and N_2, and for M = Ca when X is NH_3, PH_3, or H_2S. This point has already been noted for $MgOH_2^{2+}$ [13], where the least energy-demanding dissociative process yields $Mg^{+} + H_2O^{+}$. A complete consideration of the thermochemistry of any MX^{2+} potential energy surface must, of necessity, include such charge-separating fragmentations as well as, where feasible, proton loss. In the present work, however, we have restricted our ambit to include only calculation of the enthalpy of formation for MX^{2+} and the metal dication affinity of the ligand X, for two reasons. First, the inclusion of charge-separating fragmentation processes is only useful if the kinetic barriers to such fragmentation are also determined. In many instances, these barriers will arise at very large metal–ligand separations and the treatment of these stationary points, even by high-level procedures such as G2, may be comparatively poor. Second, the metal dication affinity of X is the parameter that is most likely to be susceptible to accurate experimental determination (and therefore, we hope, to providing a foothold which will permit attainment of accurate experimental enthalpies of formation for MX^{2+}) because association of M^{2+} with X is expected to lack any activation energy barrier. Conversely, the threshold for dissociation of MX^{2+} to $M^{2+} + X$ is therefore expected to be equal to the MDA of the ligand X [39]. Experimental techniques which could provide accurate MDA(X) values already exist [28,40,41], although they have not yet been applied to such a problem.

3.2. $M(H_2O)^{2+}$

As noted in Sec. 3.1, a majority of the previous studies on M^{2+}/ligand species has focused upon the aquo complexes $M(H_2O)_n^{2+}$ [13–23], with more studies reporting values for Mg^{2+} than for Ca^{2+}. The present G2, G2(MP2), and G2(QCI) results are nonetheless of value since they involve calculations using a higher level of electron correlation—QCISD(T)—and a larger basis—6-311+G(3df,2p)—than has been used previously for these systems. Although the lack of experimental values for the metal–ligand bond strengths prevents an unequivocal assessment of the absolute accuracy of any of the calculated values, it is reasonable to assume that the present G2(QCI) values form an acceptable “benchmark” with which the earlier results can be compared.

Our G2(QCI) value of $D(\mathrm{Mg}^{2+}–\mathrm{H_2O}) = 329.6$ kJ mol^{-1} compares with literature values of 328.0 kJ mol^{-1} (SCF/DZP) [15], 342.7 kJ mol^{-1} (SCF/TZP) [19], 355.2 kJ mol^{-1} (SCF calculation incorporating a dispersion term) [14], 368.2 kJ mol^{-1} (SCF/MIDI-4) [20], 327.2 kJ mol^{-1} (MP2/6-31G*) [23], 332.6 kJ mol^{-1} [MP2(full)/TZ2P] [18], and 326.3 kJ mol^{-1} [QCISD(T)/6-311+G**] [22]. The good agreement evident between all of the methods that include some form of electron correlation—in this case, MP2, QCISD(T), and the G2 techniques—is an encouraging indication that the calculations have already essentially converged at a comparatively low level of theory, and thus further extension of the basis set or more refined treatment of electron correlation is unlikely to yield a significantly different result. Differences between our QCISD/6-311G** geometry and those reported previously at lower levels are also small.

For $\mathrm{Ca(H_2O)^{2+}}$, our G2(QCI) calculations yield a value of 223.5 kJ mol^{-1} for the $\mathrm{Ca^{2+}–H_2O}$ bond strength. The previous values reported for this quantity are 230.1 kJ mol^{-1} (SCF/TZP) [19], 249.8 kJ mol^{-1} (SCF calculation incorporating a dispersion term) [14], 245.2 kJ mol^{-1} (SCF/MIDI-4) [20], 221.8 kJ mol^{-1} (MP2 calculations using a ten-valence-electron effective core potential for Ca and a 6-31G* basis for other atoms) [23], 217.1 kJ mol^{-1} [MP2(full)/TZ2P] [18], and 192.8 kJ mol^{-1} [MP2(FC) calculations using a $(14s, 11p, 1d)/[8s, 6p, 1d]$ contracted basis for Ca and a 6-31+G* basis for other atoms] [22]. Here also the agreement between results incorporating electron correlation is generally good, but the value reported by Magnusson [22] is significantly lower than the others. It is notable also that the geometries reported in the latter study [22] feature Ca–ligand bonds that are consistently longer (by between 0.1 and 0.2 Å) than are seen in the other studies, including the present work. We have identified the disagreement between our results and those of Magnusson as arising from the use of the standard frozen-core (FC) approximation (i.e. excluding the Ca 3s and 3p orbitals from the correlation space) in his calculations [22]. In previous studies [31,38], we have found that correlation of the Ca 3s and 3p orbitals is necessary to obtain reliable total energies and bond lengths for CaO and other species.

3.3. $\mathrm{M(NH_3)^{2+}}$

Some previous studies of the $\mathrm{M^{2+}}$/ammonia complexes have been reported [16,22]. Our G2(QCI) value of 393.0 kJ mol^{-1} for the $\mathrm{Mg^{2+}}$ bond strength compares reasonably with previous values of 388.1 kJ mol^{-1} (corrected HF/MINI-1 calculations) [16], 407.1 kJ mol^{-1} (SCF/MIDI-4) [20], and 398.0 kJ mol^{-1} (QCISD(T)/6-311+G**) [22]. Satisfactory agreement is also evident between our value of 255.1 kJ mol^{-1} for the $\mathrm{Ca^{2+}}$ bond strength and previous values of 240.6 kJ mol^{-1} (corrected HF/MINI-1 value), 253.1 kJ mol^{-1} (SCF/MIDI-4) [20], and 251.0 kJ mol^{-1} [MP2(FC)/6-31+G* calculation, with a $(14s, 11p, 1d)/[8s, 6p, 1d]$ contracted basis for Ca] [22]. The good agreement between our values and those of Magnusson [22], whose study would appear to be the only previous examination of these species to have included electron correlation in some fashion, contrasts with the discrepancy evident in the calculations on $\mathrm{Ca(H_2O)^{2+}}$. For both species, the earlier study excluded the Ca 3s and 3p orbitals from the correlation space [22]; in the case of $\mathrm{CaNH_3^{2+}}$, this appears to result in a fortuitous cancellation of errors.

3.4. $\mathrm{M(H_2S)^{2+}}$, $\mathrm{M(PH_3)^{2+}}$

These species are discussed in combination here because the existing theoretical values come from two studies [20,22] which have considered all four species. The study by Kikuchi and co-workers [20] involves SCF calculations using a modest basis set, and their MDA values are uniformly substantially lower than our results. On the other hand, agreement between our G2(QCI) results and Magnusson’s QCISD(T)/6-311+G* values for $\mathrm{Mg(H_2S)^{2+}}$ and $\mathrm{Mg(PH_3)^{2+}}$ [22] is excellent, with discrepancies of only 0.5 and 2 kJ mol^{-1}, respectively. However, significant discrepancies are evident between our G2(QCI) MDA values for $Ca(H_2S)^{2+}$ and $Ca(PH_3)^{2+}$ (173.4 and 194.7 kJ mol^{-1}, respectively) and the corresponding values of 140.5 and 168.5 kJ mol^{-1} obtained for these parameters in Magnusson's study [22]. As noted in Sec. 3.2, the low MDA values (and long Ca–ligand bonds) obtained in the earlier calculations on CaX^{2+} [22] reflect the exclusion of the Ca 3*s* and 3*p* orbitals from the correlation space in those calculations. The contrasting structures of species such as $M(H_2S)^{2+}$ and their first-row analogues [e.g. $M(H_2O)^{2+}$] has been discussed previously by Magnusson [22].

3.5. $M(HF)^{2+}$, $M(HCl)^{2+}$

The only previous study to have investigated the four dications $Mg(HF)^{2+}$, $Ca(HF)^{2+}$, $Mg(HCl)^{2+}$, and $Ca(HCl)^{2+}$ is the survey of Kikuchi et al. [20]. As in Sec. 3.4, we find that their SCF/MIDI-4 values are much lower (by between 35 and 75 kJ mol^{-1}) than our G2(QCI) MDA values for these four species.

3.6. $M(N_2)^{2+}$

Our G2(QCI) values of 173.6 kJ mol^{-1} for the Mg^{2+}–N_2 bond strength, and 90.6 kJ mol^{-1} for the corresponding binding energy in the transition structure for rotation around the N_2 ligand, are significantly higher than the values of 121.8 and 44.8 kJ mol^{-1} for these properties obtained in an earlier study [24] involving SCF calculations with a modest basis set. Considerably better agreement with our value for the linear $MgNN^{2+}$ minimum is found in an MP3/6-31G* study [25], which yielded a bond strength of 168.2 kJ mol^{-1}.

Three prior investigations of $Ca(N_2)^{2+}$ have been reported [24,25,28]. In the study by Pinchuk [24], SCF calculations provide a barrier height for ligand end-to-end rotation which is in good agreement with our own values for this parameter, although the bond strength of 79.1 kJ mol^{-1} determined in Pinchuk's study for the $CaNN^{2+}$ linear complex is markedly below our G2(QCI) value (96.6 kJ mol^{-1}) for this species. Two treatments involving electron correlation have been performed, namely a MP3/6-31G* calculation with a [5*s*, 4*p*] contracted basis for Ca [25] and an MP2/6-311+G(2*df*) calculation with a (15*s*, 11*p*, 5*d*, 1*f*)/[12*s*, 9*p*, 5*d*, 1*f*] contraction for Ca [28]. These studies have furnished bond strengths of 83.3 and 95.4 kJ mol^{-1}, respectively, in comparison with our G2(QCI) value of 96.6 kJ mol^{-1}. The basis set described above for the MP2 calculation [28] has also been used in a B3-LYP geometry optimization which yields bond lengths in reasonable agreement with our QCISD/6-311G** values for the linear minimum and for the transition structure for ligand rotation.

3.7. $M(CO)^{2+}$

Nandi and Sannigrahi [26] have reported that $MgOC^{2+}$ is the lower-energy of the two linear geometries for $Mg(CO)^{2+}$ at the HF/6-31G* level, but that the energy ordering of $MgCO^{2+}$ and $MgOC^{2+}$ is reversed upon inclusion of electron correlation. This phenomenon has also been noted by Ikuta [25], whose MP3/6-31G* values for the MDA at C and at O (205.9 and 176.6 kJ mol^{-1}, respectively) are in very good agreement with our results. Ikuta has also studied $Ca(CO)^{2+}$ where the relative energy ordering of the linear isomers parallels that found for $Mg(CO)^{2+}$. The values of 94.6 and 84.9 kJ mol^{-1} for the calcium dication affinities of CO at C and O, respectively [25], are rather lower than our values (Table 2). Significantly, neither of these earlier studies [25,26] has considered any nonlinear $M(CO)^{2+}$ geometries, nor did they report ZPE values for the linear structures, leaving somewhat open-ended the question of whether the linear structures are distinct $M(CO)^{2+}$ isomers. We have addressed this point in the present study.

In addition to the QCISD/6-311G** optimizations that were used to obtain the G2, G2(MP2), and G2(QCI) total energies for these species, we have also performed geometry optimizations for the two linear $M(CO)^{2+}$ isomers and for the transition structure for their interconversion at several lower levels of theory as detailed in Table 1. These results indicate that all geometries are fairly insensitive to basis set and correlation methods, an encouraging observation in that it implies that these species are likely to be well-treated at the levels of theory used here. The identity of both MCO^{2+} and MOC^{2+} as equilibrium structures was confirmed by vibrational frequency calculations at the HF/6-31G*, MP2/6-31G*, QCISD/6-31G*, and B3-LYP/6-31G* levels of theory.

3.8. $M(CO)^+$

We can compare our $[M–(CO)]^{2+}$ bond strengths with analogous values for monocations, and to this end we have determined standard G2 total energies for $M(CO)^+$ stationary points (as shown in Table 3) for M = Li, Na, Mg, Al, K, and Ca. Optimized geometries for these species are depicted in Fig. 2. Examination of the monocationic results indicates that there is a very close correlation between metal–ligand bond distance and bond strength for both the MCO^+ and MOC^+ geometries, with the strongest bonds (and shortest metal–ligand separations) found for Li^+ and the weakest, longest bonds found for K^+ or Al^+. In addition, MCO^+ is always found to be the preferred geometry. In all cases the $M(CO)^+$ transition structure is very weakly bound, with only Li^+ showing this stationary point to be bound by more than 4 kJ mol^{-1}. Note that we were unable to locate a $Ca(CO)^+$ transition structure at MP2/6-31G* and HF/6-31G*. However, we were able to locate this feature on the MP2(full)/6-311G** surface, and this is the level where the optimized geometry and the ZPE value has been taken.

When comparing the monocationic and dicationic results, it is immediately apparent that the $Mg(CO)^{2+}$ and $Ca(CO)^{2+}$ bond strengths are much higher than those for any of the singly charged species surveyed here. In particular, the bond strengths for Mg^{2+} and Ca^{2+} are always at least a factor of 4 times as large as those for the corresponding Mg^+ or Ca^+ monocations. This is largely attributable to electrostatic effects. It is also notable that the binding energy of the transition structure for isomerization is at least about an order of magnitude greater for $M(CO)^{2+}$ than for any $M(CO)^+$ species, and this has possible implica-

Table 3
G2 total energies, enthalpies of formation, and metal cation affinities for $M(CO)^+$ species

Species	ZPE[a]	E_0(G2)[b]	$\Delta H^\circ_{f,0}$[c]	$D(M^+ - CO)$[d]
$LiCO^+$	6.84	−120.436 74	490.5	61.5
$Li(CO)^+$ TS	5.30	−120.417 00	542.3	9.6
$LiOC^+$	6.12	−120.431 28	504.8	47.1
$NaCO^+$	6.26	−274.856 11	426.1	37.6
$Na(CO)^+$ TS	5.15	−274.843 15	460.1	3.6
$NaOC^+$	5.68	−274.851 87	437.2	26.5
$MgCO^+$	6.43	−312.558 25	719.2	43.8
$Mg(CO)^+$ TS	5.05	−312.542 56	760.4	2.6
$MgOC^+$	5.57	−312.552 16	735.2	27.8
$AlCO^+$	6.04	−354.902 28	749.6	30.8
$Al(CO)^+$ TS	5.04	−354.891 61	775.2	2.8
$AlOC^+$	5.90	−354.897 08	760.8	17.2
KCO^+	5.93	−712.449 59	356.0	24.5
$K(CO)^+$ TS	5.08	−712.441 00	378.6	2.0
KOC^+	5.51	−712.447 20	362.3	18.3
$CaCO^+$[e]	6.04	−790.025 75	622.9	29.0
$Ca(CO)^+$ TS[f]	4.66	−790.015 95	648.6	2.4[g]
$CaOC^+$[e]	5.53	−790.022 70	630.9	20.9

[a] Zero-point energy, in mHartrees (1 mHartree = 2.6255 kJ mol^{-1}), obtained as the corrected value from the HF/6-31G* geometry.

[b] Total G2 energy, in Hartrees, including ZPE.

[c] G2 enthalpy of formation, in kilojoules per mole, at 0 K.

[d] Calculated metal–ligand bond strength, in kilojoules per mole.

[e] To aid in comparison with the transition structure, we have also obtained G2 parameters for these species using MP2(full)/6-311G** optimized geometries and ZPE values [$CaCO^+$:ZPE = 5.65, $E_0 = -790.026\,91$, $\Delta H^\circ_{f,0} = 619.8$, $D(Ca^+–CO) = 31.2$; $CaOC^+$:ZPE = 5.26, $E_0 = -790.023\,20$, $\Delta H^\circ_{f,0} = 629.6$, $D(Ca^+–OC) = 21.4$].

[f] The optimized geometry and ZPE in this case were determined at the MP2(full)/6-311G** level, see text.

[g] Calculated using MP2(full)/6-311G** optimized geometries and ZPE values for all species.

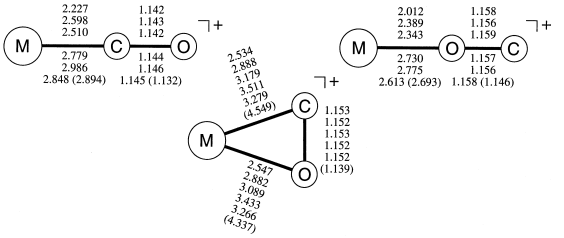

Fig. 2. Optimized geometries for $M(CO)^+$ stationary points, obtained at the MP2(full)/6-31G* level of theory [MP2(full)/6-311G** values in parentheses]. Interatomic distances, in angstroms, are shown in the order M = Li, Na, Mg, Al, K, and Ca.

tions for the interconversion of these species. If we consider that the molecular monocations and dications can each arise via an associative mechanism:

$$M^{n+} + CO \rightarrow M(CO)^{n+} \qquad (3)$$

perhaps occurring in some bath gas in a flow or drift tube, then stabilization of the monocationic collision complex $[M^{+}\cdots(CO)]^*$ by a subsequent collision with a bath gas molecule X:

$$[M^{+}\cdots(CO)]^* + X \rightarrow M(CO)^{+} + X^* \qquad (4)$$

may well quench the collision complex sufficiently to prevent further isomerization and "freeze it out" in one of the two isomeric forms. In contrast, removal of much more internal energy is required to cease all isomerization within the dicationic collision complex $[M^{2+}\cdots(CO)]^*$. We would therefore predict that the MCO^{+}:MOC^{+} ratio observed in an experimental study involving product formation by reaction (3) should correspond to the density-of-states ratio of the two isomers in the initial collision complex, whereas the MCO^{2+}:MOC^{2+} ratio is more likely instead to reflect the respective densities of rovibrational states of the two isomers at the energy of the saddle point to isomerization (substantially below the initial energy of the collision complex).

3.9. Interpretation of results

The most obvious trend evident in a perusal of Table 2 is that the metal dication affinity of any ligand is always higher for Mg^{2+} than for Ca^{2+}, as is expected in a primarily electrostatic M^{2+}/ligand interaction, because of the smaller ionic radius of the lower-mass atomic dication. The MDA values for Mg^{2+} exceed those for Ca^{2+} by a factor of ~1.5–2.0 for all of the equilibrium structures investigated here. However, this does not ensure that the magnesium-containing dications will have greater stability than their calcium-containing counterparts. The lower I.E.(Ca^{+}) value [11.871 eV compared with I.E.(Mg^{+}) = 15.035 eV] means that all of the Ca-containing complexes are thermodynamically stable, which is not true of the adducts of Mg^{2+} with NH_3, PH_3, and H_2S. As noted in Sec. 3.1, however, we have not explored the existence of kinetic barriers, or the possibility of charge separation, in the present study.

Comparison with previous calculated values for the dications studied here shows that, although the G2 thermochemical values for Mg-containing dications are generally very well reproduced by calculations at comparatively modest levels of theory, the discrepancies between G2 and lower-level-of-theory calculations [22,25] on CaX^{2+} are sometimes quite large. Almost without exception, our G2, G2(MP2), and G2(QCI) bond strengths for Ca-containing dications are larger than those obtained from other calculations that include electron correlation reported by other workers [18,22,23,25,28]. It is relevant to note in this respect that the G2 bond strengths for Ca-containing neutrals [31] are routinely lower, by ~10–20 kJ mol^{-1}, than the corresponding experimental values.

Further trends evident in our results, which are in keeping with previous surveys [20,22], are that the MDA values for both first-row and second-row hydrides decrease in traversal from group VB (N, P) to group VIIB (F, Cl), and that the MDA of a first-row hydride is larger than the MDA of the corresponding second-row hydride (HF/HCl with Mg^{2+} is an exception (Table 2), for reasons that are not clear at present). Similar trends have also been reported for the lithium [42] and sodium [43] cation affinities of the first- and second-row hydrides.

With regard to the possible laboratory investigation of these species, it is unclear whether the magnesium- or the calcium-containing dications will be more readily formed. The greater potential well depths on the $Mg^{2+} + X$ surfaces certainly favor this class of association process over $Ca^{2+} + X$, but the presence of exothermic charge transfer from Mg^{2+} in many instances provides a possible competing product channel. This may not be important for ground state, translationally "cold" Mg^{2+} (in many instances, the avoided crossing that leads to charge separation will occur at too great a distance for charge transfer to be efficient according to laboratory studies [3]) but it might well prove dominant if the collisions with X feature Mg^{2+} possessing significant electronic or translational excitation. The scope for such problems in the reaction of Ca^{2+} with X would appear to be significantly less, and so this class of association process may be the more easily studied despite a lower efficiency.

Experimental identification of MCO^{2+} and MOC^{2+} as distinct isomers may prove difficult, since the most straightforward means of studying these species (via mass spectrometry) cannot directly distinguish isomeric ions. Identification may be possible, however, with the use of some "monitor substance" X. For example, for X having a bond strength to M^{2+} which is intermediate between those in MOC^{2+} and MCO^{2+}, the following scenario may exist:

$$MOC^{2+} + X \rightarrow MX^{2+} + CO \quad (5)$$

$$MCO^{2+} + X \rightarrow \text{no reaction} \quad (6)$$

Of the other ligands X studied here, N_2 has an MDA value intermediate between CO at C and CO at O for Mg^{2+}, but unfortunately N_2 is not an appropriate monitor substance for mass-spectrometric identification of the $Mg(CO)^{2+}$ isomers since the molecular masses of CO and N_2 are identical.

4. Conclusions

Enthalpies of formation for MX^{2+} species, and metal dication affinity values for the corresponding ligands X, have been determined at levels of theory [G2, G2(MP2), and G2(QCI)] that are significantly higher than those employed previously for any of the dications in question. Very good internal consistency is evident in the results, although an absolute assessment of the reliability of these values is made difficult by an absence of accurate experimental values. In a comparison with previous results, good agreement is usually found for the Mg-containing dications, whereas larger differences are evident between the present and previous results for Ca-containing species.

Among the species studied, MCO^{2+}/MOC^{2+} (M = Mg, Ca) have been determined to be pairs of stable isomers. Bond strengths with respect to dissociation to M^{2+} and CO are considerably higher for $Mg(CO)^{2+}$ than for $Ca(CO)^{2+}$, but formation of $Mg^{+} + CO^{+}$ is the lowest energy dissociation process in the former case. Thus it transpires that both pairs of dications possess similar thermodynamic stabilities with respect to the lowest energy dissociation products. In both cases, the preferred isomer (by between 18 and 36 kJ mol^{-1}) is represented by the linear MCO^{2+} configuration. Prospects for the experimental detection of these dications appear good, although distinguishing between isomers may prove difficult.

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