

**Mass spectrometric detection of alkaline earth monohalide dications**By S. FALCINELLI†, F. FERNÁNDEZ-ALONSO, K. S. KALOGERAKIS, and  
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Quadrupole mass spectrometry has been used to detect  $\text{BaX}^{2+}$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ),  $\text{SrCl}^{2+}$ ,  $\text{CaBr}^{2+}$ , and  $\text{MgBr}^{2+}$ . Dications were produced by electron bombardment of an effusive beam containing the stable alkaline earth monohalide radical precursor. All species but  $\text{MgBr}^{2+}$  are predicted to be thermodynamically stable.  $\text{MgBr}^{2+}$  is likely to be metastable but with a lifetime sufficiently long to allow its detection in the millisecond timescale. Simple arguments are presented for the expected trends in stability.

**1. Introduction**

Consider the general diatomic dication  $\text{XY}^{2+}$ . If  $\text{XY}^{2+}$  separates into  $\text{X}^+ + \text{Y}^+$  on increasing the internuclear distance, then we expect it to dissociate because of Coulomb repulsion. On the other hand,  $\text{XY}^{2+}$  can be thermodynamically stable if upon separation it correlates with either  $\text{X}^{2+} + \text{Y}$  or  $\text{X} + \text{Y}^{2+}$  because ion–neutral interactions, the leading term in the multipole expansion for the potential energy [1], are attractive to first order. More generally, the stability of diatomic dications can be quantified by the use of the parameter  $\Delta$ , defined as

$$\Delta = \text{IP}(\text{X}^+) - \text{IP}(\text{Y}), \quad (1)$$

where IP stands for the atomic ionization potential and X corresponds to the atom with the lower first ionization potential. The parameter  $\Delta$  was introduced first by Bates and Carson [2] in 1955. From equation (1) it is clear that negative values of  $\Delta$  lead to the  $\text{X}^{2+} + \text{Y}$  curve lying below  $\text{X}^+ + \text{Y}^+$  thus ensuring thermodynamic stability. Large positive values of  $\Delta$  lead to the opposite situation and the ground state is at best metastable, i.e., the dissociation asymptote lies below the local potential energy minimum. Small positive values of  $\Delta$  may correspond to either case, depending on the depth of the potential well corresponding to the  $\text{X}^{2+} \cdots \text{Y}$  configuration. From these arguments, thermodynamically stable diatomic dications are expected between atoms with low first and second ionization potentials, i.e., divalent metal atoms like the alkaline earths, and atoms with large first ionization energies, such as the noble gases and the halogens.

Historically, the study of diatomic dications has not followed the logic presented above. Their identification was achieved first by Vaugham [3] with the discovery of  $\text{CO}^{2+}$  in 1931, even though Thompson [4] and Conrad [5] had previously suggested their existence. Since then, the rationale behind their unexpected stability has been investigated extensively. Pauling [6] was the first to carry out valence bond calculations on  $\text{He}_2^{2+}$ , a molecule isoelectronic with  $\text{H}_2$ . His work showed that  $\text{He}_2^{2+}$  was a metastable species characterized by simple covalent bonding superimposed on a

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Coulomb repulsive potential. Later, Hurley and Maslen [7, 8] developed an approximate procedure for estimating the potential energy curves of diatomic dications such as  $F_2^{2+}$ ,  $O_2^{2+}$ ,  $CO^{2+}$ , and  $NO^{2+}$  from the known electronic curves of isoelectronic neutrals. All the species studied by Hurley and Maslen displayed the same features as that of the  $He_2^{2+}$  prototype, i.e., the potential well minimum lies above the dissociation asymptote. More recent studies using high-level *ab initio* methods for  $F_2^{2+}$  [9],  $OH^{2+}$  and  $N_2^{2+}$  [10],  $O_2^{2+}$  [11],  $B_2^{2+}$  [12],  $HS^{2+}$  [13],  $CO^{2+}$  [14],  $NF^{2+}$  [15], and  $He_2^{2+}$  [16] have corroborated this picture, which is generally valid for homonuclear or slightly polarized diatomic dications.

Theory has also been complemented by experimental studies focusing on the mass spectrometric detection of dications such as  $NO^{2+}$ ,  $CO^{2+}$ ,  $N_2^{2+}$  [17],  $HS^{2+}$  [13], and  $NF^{2+}$  [18], as well as the spectroscopic characterization of  $N_2^{2+}$  and  $NO^{2+}$  [19–21]. Recently, van der Kamp *et al.* [22] reported the first study of charge-transfer reactions between  $CO^{2+}$  and  $NO^{2+}$  with alkali atoms in the investigation of quasibound states in highly excited  $CO^+$  and  $NO^+$ . Apart from charge-transfer reactions we are aware only of the work of Chatterjee and Johnsen [23] on the reaction of  $O_2^{2+}$  with  $NO$  to produce  $NO^{2+}$  and  $O^+$ . On a more practical level, other authors have been interested in these species as possible candidates for energy storage [24–26]. For example, Nicolaides [26] has proposed  $He_2^{2+}$  as a possible source of propulsive energy based on its high-energy content, low weight, and relatively long lifetime.

Little attention has been given to the possibility of thermodynamic stability in diatomic dications. The first yet profound attempt to examine the conditions necessary to attain thermodynamic stability in dications was the work of Bates and Carson which led to the parameter  $\Delta$  in equation (1) [2]. Recent interest in thermodynamically stable diatomic dications has been fostered by *ab initio* theory [25, 27–32]. Moreover, experimental evidence for their existence has been provided by Johnsen and Biondi, who observed the thermodynamically stable dication  $XeNe^{2+}$  in a drift-tube mass spectrometer as early as 1979 [33]. This species was studied later by Helm *et al.* [34] using a similar experimental scheme. Its electronic structure and properties were explained at a qualitative level using the known electronic curves of the isoelectronic neutral  $XeO$ . Similarly, Brion *et al.* [35, 36] have observed  $SiF^{2+}$  in the photoionization of  $SiF_4$ . This dication was then studied via multireference CI *ab initio* calculations by Kolbuszewski and Wright [31], who showed it to be thermodynamically stable.

Alkaline earth dications have been proposed as good potential candidates for thermodynamic stability owing to the relatively low ionization potentials of the metal atom and the closed-shell configuration of the divalent metal ion. Bates and Carson [2] predicted  $MgNe^{2+}$  to be of this type. Its detection, however, has been hampered by the lack of stable neutral precursors that may be used in charge-stripping experiments. In a more extensive *ab initio* investigation of these species, Wright and Kolbuszewski [29, 32] have proposed possible experimental schemes for the detection of dications such as  $BeF^{2+}$ ,  $MgN^{2+}$ ,  $MgO^{2+}$ ,  $MgF^{2+}$  and  $MgNe^{2+}$ .

The present paper reports the detection of a total of seven alkaline earth monohalide dications. The search, which has not been exhaustive, appears to corroborate the suggestion of Wright and Kolbuszewski that bound states are likely to exist for all combinations of alkaline earth metals and halogen atoms.

## 2. Method

The experimental setup has been described previously [37]. A high-temperature oven was used to generate an effusive beam containing alkaline earth atoms (M) and monohalide (MX) molecules in a differentially pumped chamber with background pressures between  $10^{-6}$  Torr and  $10^{-7}$  Torr. The beam was then directed into a quadrupole mass spectrometer (Extrel; 200 mm  $\times$  9.5 mm rods) where species were ionized via electron impact (Extrel ionizer, model 020-2), mass selected, and finally detected with a channeltron electron multiplier (Galileo, model 4816). Ion signals were digitized, averaged and stored in a digital storage oscilloscope (HP 5424A). Pressures in the mass spectrometer chamber ranged between  $10^{-7}$  Torr and  $10^{-8}$  Torr.

Alkaline earth monohalides were generated by mixing approximately equimolar amounts of the alkaline earth metal and the corresponding dihalide salt ( $\text{MX}_2$ ) and raising the oven temperature above their melting points. Formation of the monohalide (MX) molecules was via the gas-phase exothermic reaction shown below, a scheme universally employed in gas-phase studies of alkaline earth monohalides [37]:



Correlations between the measured ion signal and the beam were established by opening and closing the entrance of the beam into the mass spectrometer. This test was necessary to ensure that the ion signal was not caused by background (i.e., pump oil, water, etc.) present in the vacuum system despite the low operating pressures employed ( $10^{-7}$ – $10^{-8}$  Torr). Use of the isotopes of the metal and the halogen in natural abundance was essential to provide unambiguous proof of the existence of these species.

## 3. Results

Figures 1 and 2 show mass spectra for the seven alkaline earth monohalide dications we observed. Each spectrum shown is the result of averaging thirty-two oscilloscope traces. The predicted intensities based on isotopomer abundances have also been included in the plots as a further check on the identity of the spectra.

This investigation started with the detection of the barium series for which we have observed all four barium monohalide dications. The detection of strontium, calcium, and magnesium dications seems to suggest their stability is a universal phenomenon among the alkaline earth monohalides. No experiments were attempted with beryllium for safety reasons related to toxicity.

All the mass spectra are the result of subtracting two ion signals corresponding to the mass spectrometer opened and closed to the beam. This procedure was necessary to avoid potentially spurious signals arising from continuous background in the system. We also searched for the presence of the monocation ( $\text{MX}^+$ ) signals and, in all cases, it showed direct correlation with the presumed dication signals. The present experimental setup did not provide for the measurement of appearance potentials for either the monocations or dications in a fashion similar to that employed previously for the alkaline earth monohalides [38–41].

In most cases, the background levels were sufficiently low to ensure no contamination in the regions of interest. For  $\text{BaF}^{2+}$ , however, the spectrum shown is the result of subtracting a large background contribution. Despite the noise and poor line shape of the spectrum, the barium isotope abundances are evident.  $\text{BaCl}^{2+}$  also posed certain experimental difficulties. A large peak at an  $m/z$  of 88 showed a strong correlation with the beam, thus making it difficult to detect  $\text{BaCl}^{2+}$ . We attribute this

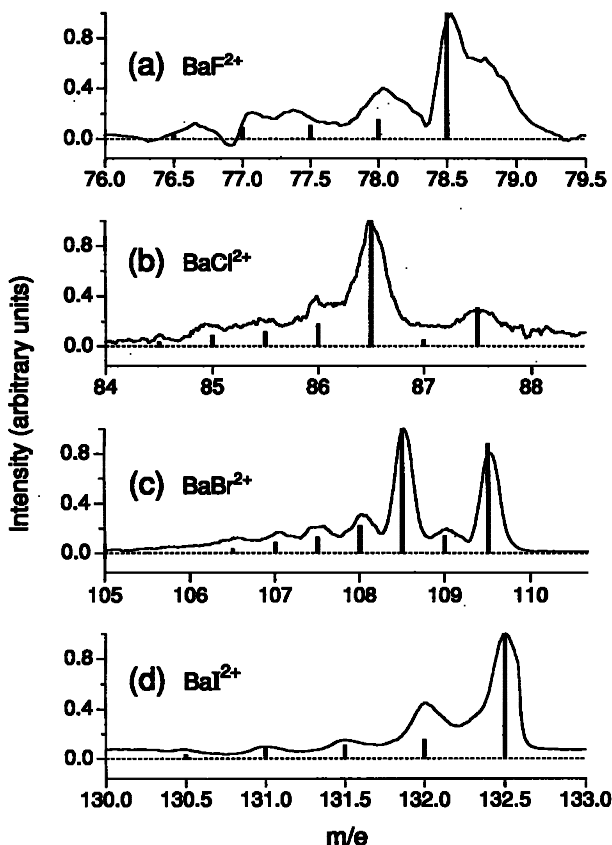


Figure 1. Mass spectra of (a)  $\text{BaF}^{2+}$ , (b)  $\text{BaCl}^{2+}$ , (c)  $\text{BaBr}^{2+}$ , and (d)  $\text{BaI}^{2+}$ . The lines show expected relative isotope intensities.

peak to a Ba-induced reaction with an unknown species at  $m/z$  39 or 40 which also showed complete correlation with the effusive beam. The  $\text{BaCl}^{2+}$  signal could be extracted from the low-mass tail of this background by recording mass spectra of this region at different temperatures above and below the melting point of  $\text{BaCl}_2$ .

Of all species investigated only  $\text{MgF}^{2+}$  proved to be elusive. It was possible to observe both  $\text{MgF}^+$  and  $\text{MgF}_2^+$ , but not  $\text{MgF}^{2+}$ . This failure, however, does not rule out its existence.  $\text{MgF}_2$  melts at 1534 K, close to the highest temperature attainable with the present apparatus. Higher temperatures or a different experimental scheme such as that used for performing spectroscopy on the alkaline earth monohalides [42–44] may prove useful in establishing its existence.

## 4. Discussion

### 4.1. Simple arguments for predicting the stability of alkaline earth monohalide dications

As discussed in the introduction, the difference in ionization potentials between  $\text{M}^+$  and  $\text{X}$  can be used to determine whether a dication is thermodynamically stable. Table 1 shows the values of  $\Delta$  for all possible combinations of alkaline earth metal atoms  $\text{M}$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ) and halogen atoms  $\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). Ionization potentials were obtained from Moore [45]. For the species pertinent to this work, most dications

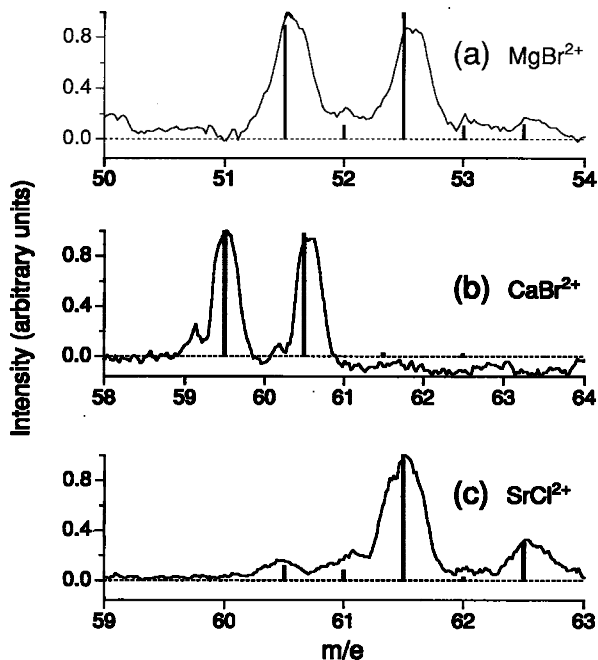


Figure 2. Mass spectra of (a)  $\text{MgBr}^{2+}$ , (b)  $\text{CaBr}^{2+}$ , and (c)  $\text{SrCl}^{2+}$ . The lines show expected relative isotope intensities.

Table 1. Values of  $\Delta$  (in eV) for the alkaline earth monohalide dications. Species pertinent to the present study are indicated in boldface.

	Be	Mg	Ca	Sr	Ba
F	0.79	- <b>2.38</b>	- 5.55	- 6.39	- <b>7.42</b>
Cl	5.24	2.07	- 1.10	- <b>1.94</b>	- <b>2.96</b>
Br	6.40	<b>3.22</b>	<b>0.06</b>	- 0.78	- <b>0.81</b>
I	7.76	4.58	1.42	0.58	- <b>0.45</b>

Table 2. Estimated potential well parameters for all the alkaline earth monohalide dications  $\text{MX}_2^{2+}$  following the approach of [49]. Table entries include the equilibrium distance  $R_m$  (in Å) followed by the well depth  $\varepsilon$  (in eV).

	Mg	Ca	Sr	Ba
F	(2.03, 0.69)	(2.49, 0.32)	(2.65, 0.27)	(2.93, 0.18)
Cl	(2.35, 1.50)	(2.77, 0.81)	(2.91, 0.68)	(3.15, 0.51)
Br	(2.45, 1.78)	(2.86, 1.00)	(2.99, 0.85)	(3.23, 0.65)
I	(2.63, 2.34)	(3.02, 1.40)	(3.15, 1.20)	(3.38, 0.95)

have negative  $\Delta$  values, which indicates that the lowest channel is  $\text{M}^{2+} + \text{X}$ . Moreover, this channel is attractive because of ion induced dipole interactions. Thus, the ground states of all species detected are expected to be thermodynamically stable except those of  $\text{CaBr}^{2+}$  ( $\Delta = +0.06$  eV) and  $\text{MgBr}^{2+}$  ( $\Delta = +3.22$  eV).

Table 2 shows potential well parameters estimated using generalized correlation formulae for ion-neutral interactions proposed by Pirani *et al.* [46–49]. These

expressions have been modified to account for the +2 charge in the metal ion. Free-ion polarizabilities were obtained from the calculations of Coker [50] and Mahan [51] and halogen polarizabilities were obtained from standard reference sources [52]. The model used to obtain the estimated equilibrium distance and well depth is purely electrostatic. It takes into account only effective dispersion ( $R^{-6}$ ) and induction ( $R^{-4}$ ) terms in the interatomic potential as a description of the attractive part. Repulsive terms in the potential are accounted for indirectly by the polarizabilities of the ion and neutral species.

The performance of this simple potential model was quite successful in reproducing the equilibrium distances for  $\text{BeF}^{2+}$ ,  $\text{MgF}^{2+}$ ,  $\text{MgNe}^{2+}$ ,  $\text{MgN}^{2+}$  and  $\text{MgO}^{2+}$  calculated from *ab initio* theory [29, 32]. The model was less successful in reproducing well depths owing to higher-order effects such as configuration-interaction mixing with other electronic states. The shortcomings of ionic models in the description of the interatomic potential of highly ionic pairs has been noted recently by Buckingham and co-workers, who calculated the dipole moments for the  $\text{Li}^+\text{F}^-$  pair [53] and the hyperfine coupling constants in alkaline earth monofluorides [54]. Despite the inherent approximations of the model used in this work, the relatively good agreement with available data seems to indicate, however, that the main contribution to the binding in doubly charged alkaline earth monohalide dications is electrostatic in nature.

The trends observed in table 2 are also in agreement with the previous discussion. Well depths increase for a given metal in going from lighter to heavier halogen atoms because of an increase in the polarizability of the latter. Analogously, well depths decrease as the size of the metal increases from Mg to Ba as a result of an increase in internuclear distance.

Despite the limitations already imposed on these estimates, the parameters listed in table 2 will prove of great utility in the examination of the stability of  $\text{CaBr}^{2+}$  and  $\text{MgBr}^{2+}$ . For highly ionic systems with positive  $\Delta$  values, Radom and co-workers have developed the AC (avoided crossing) [55] and ACDCP (avoided crossing with diabatic coupling and polarization) [56, 57] models that consider the crossing between ionic (attractive) and covalent (repulsive) diabatic curves of the same symmetry. These models have proved useful in the prediction of the avoided crossing internuclear distance and the kinetic energy release upon dissociation of diatomic dications.

Using the AC model, we can estimate the internuclear distance ( $R_{\text{ac}}$ ) where the avoided crossing between ionic and covalent curves occurs. This distance is given by the inverse of  $\Delta$  (in au). For  $\text{BeF}^{2+}$ , a well studied dication, this simple relation yields 18.2 Å, in reasonable agreement with the value of 25 Å from *ab initio* calculation [25, 29]. For  $\text{CaBr}^{2+}$ ,  $R_{\text{ac}} = 240$  Å and for  $\text{MgBr}^{2+}$   $R_{\text{ac}} = 4.5$  Å. Obviously, 240 Å is a very large internuclear distance compared with the equilibrium bond distance of 2.86 Å shown in table 2. The ionic character of the ground state of this species is corroborated further by Herzberg's classic test for ionicity, namely  $R_{\text{ac}}/R_{\text{e}} > 2$  [58]. In addition,  $\text{CaBr}^{2+}$  has an estimated well depth of 1.00 eV, which indicates further that this species is thermodynamically stable.

$\text{MgBr}^{2+}$ , on the other hand, has a repulsive asymptote 3.22 eV below the ionic curve. The predicted well depth is not deep enough and, within our approximations,  $\text{MgBr}^{2+}$  is predicted to be only metastable. It is unlikely that additional contributions to the binding energy apart from ion-induced and dispersion interactions can account for the 1.44 eV necessary to ensure thermodynamic stability. Corroboration of this conjecture will need the calculation of the electronic states by *ab initio* methods or the full spectroscopic characterization of this species. Despite its metastability,  $\text{MgBr}^{2+}$

Table 3. Values of  $\Delta$  (in eV) for other alkaline earth dications  $\text{MX}^{2+}$ . Thermodynamically stable species are indicated in boldface.

	Be	Mg	Ca	Sr	Ba
He	- <b>6.37</b>	- <b>9.55</b>	- <b>12.71</b>	- <b>13.55</b>	- <b>14.58</b>
Ne	- <b>3.35</b>	- <b>6.52</b>	- <b>9.69</b>	- <b>10.53</b>	- <b>11.56</b>
Ar	2.46	- <b>0.72</b>	- <b>3.88</b>	- <b>4.73</b>	- <b>5.75</b>
Kr	4.22	1.04	- <b>2.13</b>	- <b>2.97</b>	- <b>3.99</b>
Xe	6.08	2.91	- <b>0.26</b>	- <b>1.10</b>	- <b>2.12</b>
O	4.60	1.42	- <b>1.74</b>	- <b>2.58</b>	- <b>3.61</b>
S	7.85	4.68	1.51	0.67	- <b>0.35</b>
Se	8.46	5.29	2.12	1.28	0.25
Te	9.20	6.03	2.96	2.02	0.99
N	3.67	0.50	- <b>2.67</b>	- <b>3.51</b>	- <b>4.54</b>
P	7.21	4.04	0.87	0.03	- <b>1.00</b>

has a long lifetime that has made possible its detection. As an order-of-magnitude estimate we can use the standard formula for the rate of leakage through a potential barrier [59]. With an approximate barrier height of 1.8 eV for the diatom in the ground vibrational level and a barrier width of 4.0 Å (roughly twice  $R_{\text{ac}} - R_{\text{e}}$  where  $R_{\text{e}}$  was taken from table 2), the transmission probability becomes approximately  $e^{-800}$ . This calculation suggests a lifetime longer than a timescale of milliseconds, typical under the present experimental conditions.

#### 4.2. Other thermodynamically stable, multiply charged cations

Following the stability trends found in this work, we expected that all species listed in table 1 with negative  $\Delta$  will be thermodynamically stable. For those dications with small positive  $\Delta$  values, it is also likely that they are thermodynamically stable, as it is the case of  $\text{SrI}^{2+}$ , with  $\Delta = 0.58$  eV and a predicted well depth of 1.20 eV.

Moreover, certain combinations of alkaline earth metals and members of group VA, VIA and VIIIA also are predicted to form thermodynamically stable dications. Table 3 shows all possible combinations of atomic pairs. The number of species with negative or small  $\Delta$  values is large, suggesting once more that thermodynamic stability in diatomic dications is common. As expected from these considerations, theoretical work on  $\text{MgN}^{2+}$ ,  $\text{MgNe}^{2+}$  [32] and  $\text{BaHe}^{2+}$  [60] has shown already that all of these species are thermodynamically stable.

Similarly, we can extend our list by including group IIIB elements, which have first and second ionization potentials close to those of the alkaline earths. Table 4 shows that thermodynamic stability in these species is also a common phenomenon since nearly half of all possible dications have negative  $\Delta$  values. To our knowledge, there is only one semi-quantitative calculation for  $\text{ScN}^{2+}$ , by Kunze and Harrison [28], who found it to be thermodynamically stable by 0.53 eV.

We can also examine the possibility of thermodynamically stable triply charged diatomics by considering the combination of the noble gases and atoms with low first, second and third ionization potentials such as, for example,  $\text{YHe}^{3+}$  ( $\Delta = -4.08$  eV),  $\text{YNe}^{3+}$  ( $\Delta = -1.06$  eV),  $\text{LaHe}^{3+}$  ( $\Delta = -5.41$  eV) and  $\text{LaNe}^{3+}$  ( $\Delta = -2.39$  eV). Table 5 shows a list of group IIIB trications. Other possible candidates for thermodynamic stability are  $\text{ScHe}^{3+}$  ( $\Delta = 0.17$  eV),  $\text{ScNe}^{3+}$  ( $\Delta = 3.19$  eV),  $\text{LaF}^{3+}$  ( $\Delta = 1.75$  eV), and  $\text{YF}^{3+}$  ( $\Delta = 3.08$  eV). This conjecture requires further corroboration.

Table 4. Values of  $\Delta$  (in eV) for group IIIB dications. Thermodynamically stable species are indicated in boldface.

	Sc	Y	La
He	-11.69	-12.18	-13.15
Ne	-8.67	-9.16	-10.13
Ar	-2.87	-3.36	-4.33
Kr	-1.11	-1.60	-2.57
Xe	0.76	0.27	-0.70
F	-4.53	-5.02	-5.99
Cl	-0.08	-0.57	-1.54
Br	1.08	0.59	-0.38
I	2.44	1.95	0.98
O	-0.72	-1.21	-2.18
S	2.53	2.04	1.07
Se	3.14	2.65	1.68
Te	3.88	3.39	2.42
N	-1.65	-2.14	-3.11
P	1.89	1.40	0.43

Table 5. Values of  $\Delta$  (in eV) for other group IIIB trications. Thermodynamically stable species are indicated in boldface.

	Sc	Y	La
He	0.17	-4.08	-5.41
Ne	3.19	-1.06	-2.39
Ar	9.00	4.75	3.42
Xe	10.75	6.50	5.17
Kr	12.62	8.37	7.04
F	7.33	3.08	1.75
Cl	11.78	7.53	6.20
Br	12.94	8.69	7.36
I	14.30	10.05	8.72
O	11.14	6.89	5.56
S	14.39	10.14	8.81
Se	15.00	10.75	9.42
Te	15.74	11.49	10.16
N	10.21	5.96	4.63
P	13.75	9.50	8.17

Finally, because fourth ionization potentials are larger than the first ionization potential of any element, no tetracationic diatomics are predicted to be stable in the thermodynamic sense.

## 5. Conclusion

Mass spectrometry has been used to detect seven alkaline earth monohalide dications. Their stability has been explained in terms of simple and highly intuitive bonding models. Of all the species studied only  $\text{MgBr}^{2+}$  is metastable. The rest are predicted to be thermodynamically stable.

The same principles can be applied for the prediction of unknown dications and trications between alkaline earth or group IIIB elements and atoms from groups VA, VIA, VIIA, and VIIIA.



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