

Theoretical Study of Doubly Charged $[X(H_2O)]$ and $[X(NH_3)]$ ($X = Si, Ge, Sn, Pb$) Molecular Ions*

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Abstract. *Ab initio* calculations have been used to study the structure and stability of several doubly charged molecular ions in the gas phase. In particular the complexes of water and ammonia with Si^{2+} , Ge^{2+} , Sn^{2+} and Pb^{2+} have been studied. Geometries have been obtained at B3LYP/6-31G(d) level and final energies at CCSD(T)/6-311+G(3df,2p) level. Different fragmentation channels have been considered. The loss of X^+ ($X = Si, Ge, Sn, Pb$) is the most favorable one, except for $[Si(H_2O)]^{2+}$ where the loss of a H^+ has a lower energy cost. Water complexes are thermodynamically stable, while loss of X^+ in ammonia complexes are exothermic processes. In ammonia complexes a Coulomb barrier prevents the systems from spontaneous dissociation; to obtain these barriers the potential energy curves for the loss of Si^+ or Pb^+ in $[Si(NH_3)]^{2+}$ and $[Pb(NH_3)]^{2+}$ complexes have been obtained at CCSD(T)/6-311+G(3df,2p) level, the corresponding vibrational states have been located and their lifetimes evaluated using the exterior complex scaling. The barriers for dissociation of $[X(NH_3)]^{2+}$ complexes are similar to the ones obtained for $[X(H_2O)]^{2+}$ complexes.

Keywords: DFT calculations, molecular ions, complexes, fragmentation, dissociation

INTRODUCTION

Multiply charged species are quite common in chemistry either as ingredients of ionic compounds or as solvated species, because they are stabilized either by the crystal environment or by the solvent. However, they are rare in the gas phase, where these stabilizing interactions cannot take place. As a consequence, they exhibit very often quite short lifetimes and usually elude experimental detection. Actually, in the simplest molecular case, *i.e.*, in the case where we have a diatomic doubly charged species, $[AB]^{2+}$, if the lowest dissociation asymptote corresponds to either $A^{2+} + B$ or $A + B^{2+}$ the species will be thermodynamically stable. In other words, a $[AB]^{2+}$ species would be thermodynamically stable provided that the ionization energy (E_i) of A^+ is smaller than the E_i of B , or *viceversa*, if the E_i of B^+ is smaller than that of A .^{1,2} When this condition is not fulfilled, the system will eventually dissociate into the corresponding singly charged species, $A^+ + B^+$, in a typical Coulomb explosion. Nevertheless, an $[AB]^{2+}$ doubly charged species can still be thermodynamically stable if the binding energy in the complex compensates the differences in the E_i of A^+ and B (or B^+ and A).¹ Also the complexes can be stable (kinetically stable) if the bar-

rier, usually associated with the aforementioned Coulomb explosion, is high enough to accommodate one or more resonant vibrational levels below the top of the barrier.^{1,3,4} A quite complete discussion on the different possibilities associated with the thermodynamic or kinetic stability of doubly charged diatomic systems can be found in a feature article by Schröder and Schwarz.¹

The generation of doubly charged species in the gas phase by attachment of a dication to a neutral system was achieved in 1972 by Spears and Fehsenfeld.⁵ Nevertheless it has not been an easy task in the past, because of the need of producing the doubly charged species in a low vibrational level. The advent of electro-spray ionization techniques allowed easy production of doubly and multiply charged species in the gas phase from aqueous solution,⁶ and the unimolecular reactions of doubly charged species generated, for instance, by alkaline-earth metal dication association to neutral compounds, could be studied.^{7–10}

In general the stability of these doubly charged adducts in the gas phase should increase with the size of the system, since this would favor the delocalization of the charge within the system minimizing the effectiveness of the Coulomb explosions. However, there was

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

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some controversy on the possibility of forming stable doubly charged species by associating metal dications to small molecules like water or ammonia.^{11,12} Zvonko Maksić *et al.*,⁴ made an important contribution in this field by showing that alpha particles can be attached to small organic molecules, such as HCN or its isomer HNC, to yield doubly charged molecular ions with long lifetimes. They actually showed that although $[HNC-He]^{2+}$ and $[HCN-He]^{2+}$ species are thermodynamically unstable with respect to the loss of H^+ , the activation barriers associated with these processes are high and wide enough to accommodate several resonant states, with negligible small energy widths, below the top of the barrier.

The existence of $[Cu(H_2O)]^{2+}$ and $[Fe(H_2O)]^{2+}$ complexes have been experimentally proved,^{3,13,14} and other doubly charged metal-water complexes $[M(H_2O)]^{2+}$ ($M = Mn, Ni, Zn$) have been detected experimentally.¹³ The lifetimes of these kinds of complexes, as well as those involving NH_3 and HCN, estimated by high-level *ab initio* calculations, are so large that they should actually behave as normally bound species.¹⁵

Also recently, experimental evidence for the existence of $[Pb(H_2O)]^{2+}$ together with *ab initio* calculations, which showed that this species is thermodynamically stable, were reported in the literature.^{16,17} These findings prompted us to investigate whether a similar behavior can be expected for other simple bases, such as ammonia, and whether other dications of the same group, but lighter than Pb, can also yield stable (thermodynamically or kinetically) doubly charged ions when associated with small molecules. For this purpose we chose Si^{2+} , Ge^{2+} , Sn^{2+} and Pb^{2+} to study the variation of the stability along the group.

COMPUTATIONAL DETAILS

In order to have a description of the structure of the complexes formed, we have fully optimized the geometries of $[X(H_2O)]^{2+}$ and $[X(NH_3)]^{2+}$ ($X = Si, Sn, Ge, Pb$) using Density Functional Theory (DFT). The B3LYP functional combined with a 6-31G(d) has been used for geometry optimization. This level of theory is known to give accurate results for the geometries of a wide variety of systems in particular for complexes of metal cations with organic bases.¹⁸⁻²² We have checked that the spin contamination is negligible in the species with a doublet multiplicity.

All electrons have been considered in the calculations with Si and Ge, while in the case of Sn and Pb we have used effective core potentials to describe the inner electronic shells. In the case of Sn the potential proposed by Stevens *et al.*²³ has been used while for Pb the

one proposed by the Stuttgart group²⁴ has been employed. Two different basis set of the same quality, the 6-31G(d) and 6-311+G(3df,2p), have been used for the geometry optimization and final energy calculations respectively, the details of these basis set have been previously described for Sn²⁵ and Pb²⁶.

Atomic charges have been evaluated by means of Natural Bond Orbital theory²⁷ using the densities evaluated at the B3LYP/6-311+G(3df,2p) level over B3LYP/6-31G(d) optimized geometries. Final energies have been refined by performing single point calculations at CCSD(T)/6-311+G(3df,2p) level of theory on the B3LYP/6-31G(d) optimized geometries. All calculations have been performed using the Gaussian 03 suite of programs.²⁸

As we will discuss later, in the case of ammonia complexes the most stable dissociation limit corresponds to the dissociation into X^+ and NH_3^+ and it lies below in energy than the $[XNH_3]^{2+}$ complex. A Coulomb barrier prevents the system for undergoing spontaneous explosion into both fragments. In order to discuss the stability of the complex, it is necessary to have an estimate of the number of vibrational levels that exists in the potential energy well below the top of the barrier and their lifetimes. These levels are metastable and therefore appear as resonances embedded in the vibrational continuum. Therefore we have obtained the complete potential energy curve for X^+ dissociation. These curves have been obtained by fixing the N-X distance at different values and optimizing the rest of parameters at the CCSD/6-31G(d) level. Final energies for each point have been obtained at the CCSD(T)/6-311+G(3df,2p) level using the corresponding optimized geometry. The two fragments produced have a total spin multiplicity of 2, but the total spin multiplicity of the complex remains singlet. Since such a fragmentation cannot be described by a monodeterminantal wavefunction, it is normal to expect that the HF calculation will become unstable at large N-X distances and therefore CCSD(T) calculations will be also unreliable. At those distances at which the HF becomes unstable we have assumed that the potential energy curve follows a Coulomb potential leading asymptotically to the $X^+ + NH_3^+$ dissociation limit.

The positions and lifetimes of the resonances in these potential energy curves have been evaluated using a recent implementation of the exterior complex scaling (ECS) method with complex B-spline functions.²⁹ The ECS transformation scales the dissociation coordinate outside a fixed radius R_0 within which the continuum wave function satisfies the usual scattering boundary conditions. As a result of this, the eigenvalues associated with resonance states are complex. The corresponding real and imaginary parts provide, respectively,

the energy position E_r and the inverse of twice the lifetime $2/\Gamma$ of the resonance (we call Γ the resonance width). The B-splines that scale according to this ECS transformation are defined by setting a series of knots on the complex contour and by using the usual recursion relation³⁰ for the real B splines of order k . In this way, ECS benefits from the practical completeness of B-spline basis sets to provide almost exact results. The details of this implementation have been discussed at length in Ref. 29.

RESULTS AND DISCUSSION

We have considered the doubly charged complexes $([X(H_2O)]^{2+}$ and $[X(NH_3)]^{2+})$, and four different dissociation channels (the molecules or complexes produced in each channel are given in parentheses): a) loss of X^{2+} (H_2O or NH_3); b) loss of X^+ (H_2O^+ or NH_3^+); c) loss of H^+ ($[X(OH)]^+$ or $[X(NH_2)]^+$ complexes) and d) loss of H ($[X(OH)]^{2+}$ or $[X(NH_2)]^{2+}$ complexes). All the species indicated in parentheses have been fully optimized. Neutral and singly charged $[X(H_2O)]$ and $[X(NH_3)]$ complexes have been also considered for completeness and comparison purposes.

The optimized geometries at B3LYP/6-31G* level of all these molecules are summarized in Table 1 and the corresponding atomic charges are indicated in Table 2. The distances obtained in the Pb complexes are much shorter than the ones obtained in Ref. 31 for $[Pb^{II}-4H_2O]$ and $[Pb^{II}-4NH_3]$ (2.460 and 2.620 Å respectively) and the electronic charge transferred to the Pb lower. For NH_3 and H_2O complexes the X–N and the X–O bonds are reinforced by a significant amount (the bond distance decreases by 0.2 Å) when increasing the charge of the system. In contrast the N–H and O–H bonds are weakened when increasing the total charge. These effects can be easily explained by looking at the atomic charge populations (Table 2). For NH_3 and H_2O complexes the charge on the N (or O) remains practically constant and negative independently of the total charge of the system, while the H atoms are positively charged. These charges reflect the polarity within the NH_3 and H_2O molecules. Importantly, however, the total charge of the complex is practically located on the metal and therefore the charge-dipole interaction increases when increasing the charge on the metal, leading to a reinforcement of the X–N (and X–O) bonds.

The opposite trend is found for the complexes in which a H has been lost, *i.e.* $[X(NH_2)]$ and $[X(OH)]$ complexes. The X–N and X–O bonds enlarge when increasing the charge of the system. The analysis of the NBO charges (Table 2) shows that in these cases a sig-

nificant electronic charge is transferred in the monocations from the metal to the O (or N), being the charge on the metal in the monocations larger than 1.5. In the dications the charge on the metal is lower than 2 and the negative charge on the O (or N) is significantly reduced. As a consequence the interaction between the OH (or NH_2) and the metal is weaker for the dications.

The large interaction between the metal and the NH_2 or OH in the monocations is also reflected in very short X–N or X–O distances, these distances being 0.3–0.4 Å shorter than the corresponding distances in the $[X(NH_3)]^+$ or $[X(H_2O)]^+$ species. For the dications, and with the exception of $[Si(OH)]^{2+}$, the opposite is found; the X–N or X–O distances are longer than in the $[X(NH_3)]^{2+}$ or $[X(H_2O)]^{2+}$ complexes.

It is also worth noting that in the case of the $[X(NH_2)]$ complexes both cations and dications present a planar C_{2v} symmetry. For $[X(OH)]$ complexes the cation is always more stable in the linear form, while in the case of the dications there is a competition between the linear shape and the angular one, the difference in energy between both conformations is very small, of the order of 0.1 eV. In the case of Si and Pb complexes the angular form is the most stable one, while for Ge and Sn the angular form is not stable and evolves to the linear one.

The stabilities of the $[X(NH_3)]^{2+}$ and $[X(H_2O)]^{2+}$ complexes can be discussed in terms of the dissociation energies defined in Figure 1 and summarized in Table 3. According to Figure 1, the critical quantity to determine the stability of the complexes and to interpret charge-stripping experiments is the position of the crossing between the potential energy curves leading to the dissociation in $X^+ + H_2O^+$ (or NH_3^+) and $X^{2+} + H_2O$ (or NH_3). The position of the crossing is mainly given by the first E_i of water (and ammonia) and the second E_i of the metal. Comparison with the available experimental data³² (see Table 3) reveals that the first E_i of water and ammonia have errors lower than 0.1 eV. The errors in the first E_i of Si, Ge, S and Pb are much larger, but the second E_i s are reasonably reproduced (errors lower than 0.3 eV) for Si and Ge. The larger errors on the second E_i are obtained for Sn (0.5 eV) and Pb (1.7 eV). Attending to these results we could expect an error in the relative positions of the energy curves leading to the different dissociation limits of the order of 0.3 eV in the case of Si and Ge and significantly larger for Pb.

The lowest-lying dissociation channel is the Coulomb explosion into $X^+ + NH_3^+$ (or H_2O^+), this channel lies lower in energy than the one corresponding to the loss of a H^+ , *i.e.* the X–N (or X–O) bond is broken more easily than the N–H (or O–H) bond.

Table 1. Structural parameters obtained at B3LYP/6-31G(d) level for all the species considered in this study (distances expressed in Å and angles in degrees)

	Si			Ge			Sn			Pb		
	Neutral	Cation	Dication	Neutral	Cation	Dication	Neutral	Cation	Dication	Neutral	Cation	Dication
X-NH ₃	X-N	2.144	2.048	2.244	2.153	2.079	2.475	2.372	2.286	2.636	2.515	2.428
	N-H	1.020	1.028	1.019	1.026	1.040	1.019	1.025	1.036	1.018	1.024	1.032
	X-N-H	114.6	113.0	113.6	112.0	113.1	110.3	112.1	113.5	110.8	111.9	113.3
X-OH ₂	X-O	2.036	1.924	1.829	2.039	1.969	2.359	2.244	2.148	2.562	2.420	2.318
	O-H	0.971	0.981	1.005	0.978	0.998	0.969	0.976	0.992	0.968	0.974	0.986
	X-O-H	124.6	125.0	126.0	124.8	126.1	125.4	125.8	126.6	125.9	126.1	126.7
X-NH ₂	X-N	-----	1.670	1.985	-----	1.784	-----	1.942	2.313	-----	2.066	2.443
	N-H	-----	1.025	1.047	-----	1.023	-----	1.022	1.038	-----	1.020	1.036
	X-N-H	-----	124.8	124.8	-----	124.5	-----	125.4	125.4	-----	125.2	125.6
X-OH	X-O	-----	1.558	1.611	-----	1.693	-----	1.815	2.249	-----	1.951	2.447
	O-H	-----	0.971	1.017	-----	0.973	-----	0.970	1.007	-----	0.969	1.001
	X-O-H	-----	180.0	134.9	-----	180.0	-----	180.0	180.0	-----	180.0	141.2

Table 2. Charges obtained by means of NBO analysis at B3LYP/6-311+G(3df:2pd)//B3LYP/6-31G(d) level for all the species considered in this study

	Si			Ge			Sn			Pb		
	Neutral	Cation	Dication	Neutral	Cation	Dication	Neutral	Cation	Dication	Neutral	Cation	Dication
X-NH ₃	X	-0.14	0.82	1.80	0.82	1.79	-0.10	0.87	1.86	-0.09	0.88	1.87
	N	-1.06	-1.14	-1.30	-1.12	-1.24	-1.06	-1.13	-1.25	-1.05	-1.11	-1.21
	H	0.40	0.44	0.50	0.43	0.48	0.39	0.42	0.47	0.38	0.41	0.45
X-OH ₂	X	-0.08	0.88	1.85	0.89	1.86	-0.05	0.93	1.92	-0.04	0.95	1.93
	O	-0.95	-1.01	-1.10	-1.00	-1.08	-0.96	-1.01	-1.10	-0.95	-1.00	-1.07
	H	0.52	0.56	0.63	0.55	0.61	0.50	0.54	0.59	0.49	0.53	0.57
X-NH ₂	X	-----	1.50	1.78	-----	1.47	-----	1.58	1.87	-----	1.57	1.88
	N	-----	-1.41	-0.72	-----	-1.36	-----	-1.43	-0.72	-----	-1.39	-0.70
	H	-----	0.46	0.47	-----	0.45	-----	0.43	0.43	-----	0.41	0.41
X-OH	X	-----	1.61	2.26	-----	1.61	-----	1.71	1.94	-----	1.72	1.94
	O	-----	-1.20	-0.91	-----	-1.20	-----	-1.27	-0.51	-----	-1.26	-0.47
	H	-----	0.60	0.65	-----	0.59	-----	0.56	0.57	-----	0.54	0.53

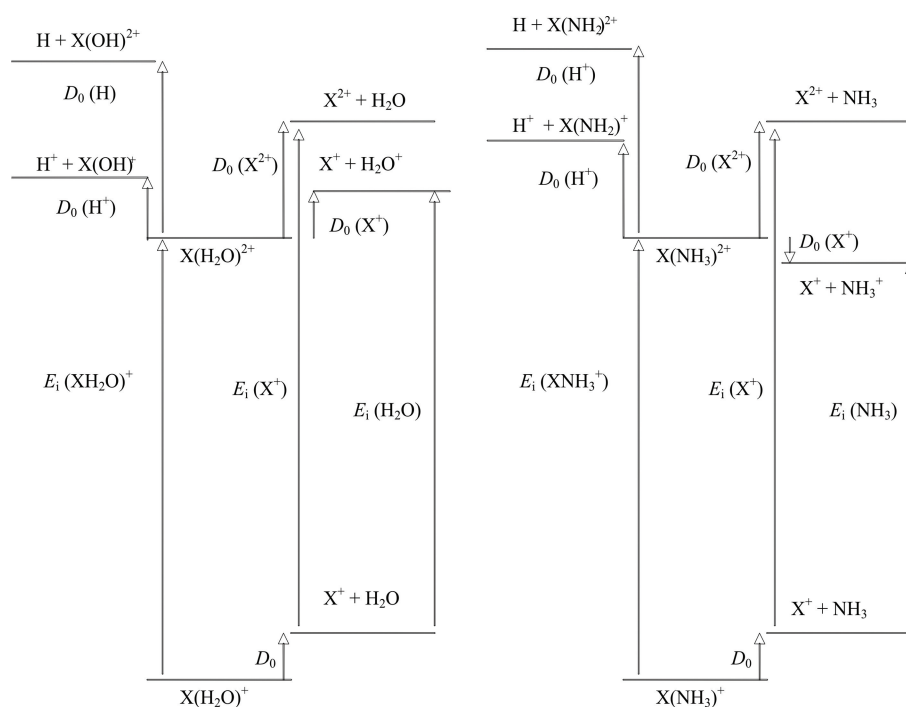


Figure 1. Born-Haber diagrams associated with the formation of $[X(NH_3)]^{2+}$ and $[X(H_2O)]^{2+}$ complexes. All the possible dissociation processes and their relative energy positions are shown. Values of all the dissociation energies (D_0) and ionization energies (E_i) are given in Table 3.

Table 3. Ionization energies (E_i) and dissociation energies (D_0) for the different channels considered (see Figure 1)^{(a),(b)}

	Si	Ge	Sn	Pb
$E_i(X)$	7.2 (8.2)	6.9 (7.9)	6.5 (7.3)	6.1 (7.4)
$E_i(X^+)$	16.2 (16.3)	15.6 (15.9)	14.1 (14.6)	13.3 (15.0)
$E_i(X(H_2O))$	5.7	5.7	5.5	5.3
$E_i(X(H_2O)^+)$	13.9	13.7	12.7	12.2
$D_0(X^+ + H_2O)$	2.0	1.7	1.4	1.1
$D_0(X^+ + H_2O^+)$	0.6 / 3.0	0.6 / 2.6	1.2 / 2.2	1.5 / 1.9
$D_0(X^{2+} + H_2O)$	4.3	3.6	2.8	2.3
$D_0(H^+ + X(OH)^+)$	0.5	1.7	2.9	3.9
$D_0(H + X(OH)^{2+})$	6.6	6.5	6.2	6.1
$E_i(X(NH_3))$	5.6	5.5	5.3	5.1
$E_i(X(NH_3)^+)$	13.6	13.3	12.4	11.9
$D_0(X^+ + NH_3)$	2.6	2.2	1.8	1.5
$D_0(X^+ + NH_3^+)$	-0.9 / 2.2	-0.9 / 2.7	-0.5 / 2.4	-0.2 / 2.5
$D_0(X^{2+} + NH_3)$	5.2	4.6	3.5	3.0
$D_0(H^+ + X(NH_2)^+)$	1.8	2.7	3.9	4.7
$D_0(H + X(NH_2)^{2+})$	5.6	5.5	5.4	5.3

^(a) All values (expressed in eV) have been obtained at the CCSD(T)/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory. Experimental values³² are given in parentheses.

^(b) The corresponding first ionization energies of water and ammonia are 12.6 eV (experimental value 12.621) and 10.1 eV (experimental value 10.070). For $X^+ + H_2O^+$ and $X^+ + NH_3^+$ dissociations, the second number corresponds to the estimated values of the energy barrier.

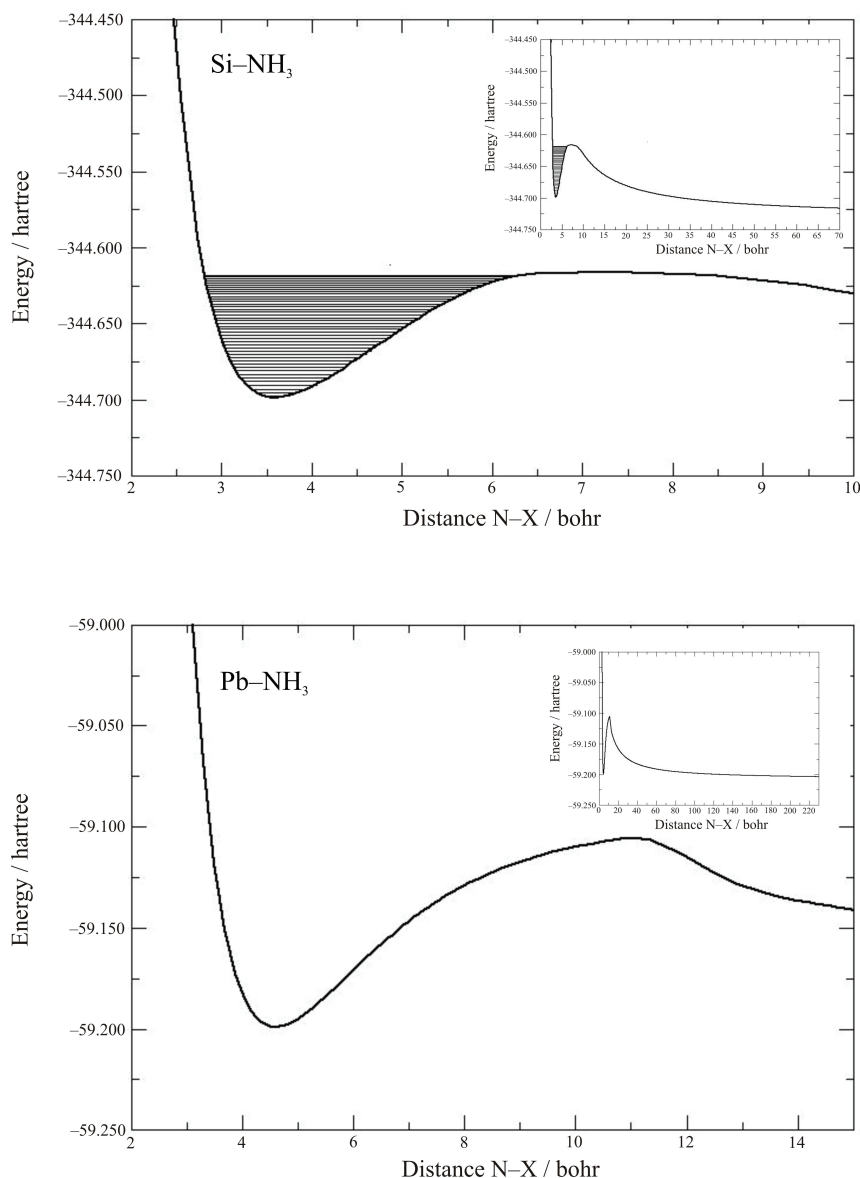


Figure 2. Potential energy curves for the dissociation of the N-X bond in $[\text{Si}(\text{NH}_3)]^{2+}$ and $[\text{Pb}(\text{NH}_3)]^{2+}$ complexes. The vibrational resonances are shown in the case of $[\text{Si}(\text{NH}_3)]^{2+}$. In $[\text{Pb}(\text{NH}_3)]^{2+}$ and due to the high mass of Pb they are not shown because they are too close to each other to be seen in the scale of the graphic. The insets show the shape of the potential energy curves at longer distances, close to the dissociation limit.

The only exception to this rule is $[\text{Si}(\text{H}_2\text{O})]^{2+}$ for which the loss of H^+ is slightly more favourable, by 0.1 eV, than the loss of Si^+ . The preference for the loss of X^+ with respect to the loss of H^+ increases when descending in the group; in the case of water complexes the loss of Ge^+ , Sn^+ , and Pb^+ are respectively 1.1, 1.7 and 2.4 eV more favourable than the corresponding loss of H^+ . Similar trends are observed for the ammonia complexes. In this case the difference in energy of the chan-

nels leading to the loss of X^+ or H^+ is enhanced (from 2.7 eV for Si^+ to 4.9 eV for Pb^+).

The most important difference between water and ammonia complexes is that in the case of water the loss of X^+ is an endothermic process, while for ammonia it is exothermic. It has to be mentioned that according to the previous discussion of the accuracy of the E_{is} , the values for the dissociation energies of $[\text{X}(\text{H}_2\text{O})]^{2+}$ complexes

are higher than the expected errors, so we can be confident in our results that predict the reactions to be endothermic. In the case of the $[X(NH_3)]^{2+}$ ($X = Si, Ge$) the value of the dissociation energy is larger than the expected error in the curves, therefore our conclusion that the reaction is exothermic in these cases is expected to be accurate. For Pb the reaction is predicted to be exothermic by only 0.2 eV. This value is below the expected error in our calculations, so in this case a higher level of theory should be performed to ensure the exothermicity of the process.

In all cases a Coulomb barrier prevents the system for fragmentation. In order to evaluate the height of the corresponding barrier we have calculated for Si and Pb the corresponding potential energy curves for the loss of Si^+ and Pb^+ (see Figure 2). As indicated in the previous section the calculation were carried out at CCSD(T)/6-311+G(3df,2p) level using CCSD/6-31G(d) geometries. CC methods are based in the HF wavefunction and for relatively long X–N distances (6.6 a_0 for Si and 11.1 a_0 for Pb) the HF wavefunction becomes unstable. As can be seen in Figure 2 at these distances the gradient of the curves is close to zero and should be near to the top of the energy barrier. Therefore we can have a good estimate of their heights: 2.2 eV for Si and 2.5 eV for Pb. For the other complexes we do not present the complete energy curve, but we have estimated in a similar way the corresponding energy barriers and the values have been included in Table 3.

Figure 2 also shows the position of the vibrational resonances in the potential energy wells of $[Si(NH_3)]^{2+}$. As can be seen, many vibrational states, up to 42, exist. The lifetimes of the upper vibrational level is 6.3×10^{-12} s according to the ECS calculations. The next level has a lifetime of 3.1×10^{-9} s and the third one from the top presents a lifetime higher than a second. The rest of the resonances present very long lifetimes, which can be considered in practice as infinite time. In the case of Pb the complex is even more stable, not only because the potential well is slightly deeper, but also because due to the higher mass of Pb the vibrational resonances are closer to each other.

An interesting conclusion is that even though the dissociation of $[X(NH_3)]^{2+}$ is an exothermic process, the dissociation curve present a high energy barrier. In fact these barriers are higher than the dissociation energies of the thermodynamically stable water complexes. $[X(H_2O)]^{2+}$ and $[X(NH_3)]^{2+}$ complexes present similar energy barriers for dissociation.

Finally, the channels leading to doubly charged fragments (X^{2+} , $[X(OH)]^{2+}$ or $[X(NH_2)]^{2+}$) also have been considered, but they are higher in energy than the one leading to the loss of X^+ . It has to be noted that

while the energy of the channel leading to dissociation of $[X(OH)]^{2+}$ or $[X(NH_2)]^{2+}$ remains constant when going from Si to Pb, the channels dissociating into X^{2+} get stabilized by 2 eV when going from Si to Pb, reflecting the lowest E_i of the Pb^+ . As a consequence these channels become more stable than the ones leading to the loss of H^+ in the complexes of Sn^{2+} and Pb^{2+} with both water and ammonia.

CONCLUSION

Theoretical calculations reveal that all the complexes formed by Si, Ge, Sn and Pb dications with water or ammonia behave as stable species in the gas phase. The complexes with water are thermodynamically stable, the preferable dissociation channel being the loss of X^+ , except for $[Si(H_2O)]^{2+}$ where the loss of a H^+ is slightly more favourable. The dissociation limit lies above the energy of the corresponding complexes. In the case of ammonia complexes the lowest dissociation channel is always the loss of X^+ and lies lower in energy than that of the corresponding complex, *i.e.* the complexes are thermodynamically unstable. However, they display a high kinetic stability due to the presence of a Coulomb barrier of the order of 2.2 to 2.5 eV. As a consequence many resonant vibrational states showing very high lifetimes are located below the top of the barrier.

The ejection of X^{2+} becomes the second most stable dissociation channel for Sn and Pb in both water and ammonia complexes. For Si and Ge the loss of a H^+ is more favourable than the loss of Si^{2+} or Ge^{2+} .

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SAŽETAK**Teorijska studija dvostruko nabijenih molekularnih iona
[X(H₂O)] i [X(NH₃)] (X = Si, Ge, Sn, Pb)****Pablo López-Tarifa, Fernando Martín, Manuel Yáñez i Manuel Alcamí***Departamento de Química, C-9. Universidad Autónoma de Madrid. 28049 Madrid. Spain*

Korišteni su *ab initio* računi za proučavanje strukture i stabilnosti nekoliko dvostruko nabijenih molekularnih iona u plinskoj fazi. To se posebice odnosi na komplekse vode i amonijaka sa Si^{2+} , Ge^{2+} , Sn^{2+} i Pb^{2+} ionima. Geometrije kompleksa dobivene su pomoću B3LYP/6-31G(d) metode a konačne energije uz pomoć CCSD(T)/6-311+G(3df,2p) nivoa teorije. Različiti fragmentacijski kanali uzeti su u obzir. Gubitak X^+ (X = Si, Ge, Sn, Pb) je najstabilniji put osim za $Si(H_2O)^{2+}$ gdje gubitak H^+ iziskuje manje energije. Kompleksi s vodom su termodinamički stabilni, dok je gubitak X^+ u kompleksima amonijaka egzotermni proces. U kompleksima amonijaka Coulombska barijera sprječava sistem od spontane disocijacije. Da bi izračunali te barijere, krivulje potencijalne energije za gubitak Si^+ i Pb^+ u $[Si(NH_3)]^{2+}$ i $[Pb(NH_3)]^{2+}$ kompleksima dobivene su na CCSD(T)/6-311+G(3df,2p) nivou teorije, a odgovarajuća vibracijska stanja locirana i njihova vremena života određena koristeći metodu modeliranja vanjskog kompleksa (engl. *exterior complex scaling method*). Barijere za disocijaciju $[X(NH_3)]^{2+}$ kompleksa slične su onima dobivenim za $[X(H_2O)]^{2+}$ komplekse.