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Original Scientific Paper

Paradigms of Dipole-bound Negative Ion States in Diatomics with High Spin Multiplicity

*Josef Kalcher**

Karl-Franzens-University, Institute for Chemistry / Theoretical Chemistry,
Strassoldogasse 10, A-8010 Graz, Austria

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Dipolar electron binding to the diatomics SiBe, SiMg, CNa, and SiNa with high-spin neutral ground states is surveyed. All molecules possess one or more valence-excited anion states. $SiNa^-$ supports at least two $^5\Sigma^-$ dipole-bound anion states. The triplet-quintet multiplet splitting of the dipole-bound states in CNa^- is rather small.

Key words: negative ion, dipole-bound states, excited states.

INTRODUCTION

Negative ions differ from neutral molecules and cations in various aspects. Small electron binding energies, which are associated with the small electron affinities of the corresponding neutral molecules, the finite number of bound electronic states, the frequently observed high sensitivity of the electron binding on the molecular geometry should be especially noted. These and several other features inspired a plethora of experimental and theoretical investigations and made negative ion chemistry a bourgeoning field during the last decades. The essential properties of gas phase anions have been reviewed quite extensively.[1–6]

Special interest in dipolar electron binding to polar neutral molecules has been steadily growing in recent years. Even astrophysicists speculate that a large portion of the so-called free electrons in space might be engaged in dipole-bound states. The theory of this special type of electron binding,

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* (E-mail: josef.kalcher@kfunigraz.ac.at)

where the extra electron is trapped by the dipolar field of the neutral parent dates back to the investigations of Fermi and Teller,[7] who pointed out that a minimal dipole moment of 1.625 D is required for dipolar electron attachment. Highly polar molecules like alkali hydrides and alkali halides are well-known supporters of such dipole-bound anion states. The purely dipolar approach[7] involves only the dipole moment and leaves all specifities of the individual molecule unconsidered. Elaborate investigations revealed, however, that such a simplistic approach is not well-suited to physical systems, where electron repulsion and electron correlation effects are operative. These effects lead to a significantly higher »physical limit« of 2–2.5 D for the actual dipole moments, and are responsible for notable individualities of the dipolar binding energies in different molecules. A plausible theoretical model of electron binding by dipole- or even higher multipole fields has been devised by Abdoul-Carime and Desfrançois.[8]

Small molecules have been theoretically investigated by Gutsev *et al.*,[9–10] calculations on nucleic acid bases have been performed by the group of Adamowicz,[11–13] and organic molcules like aldehydes and ketones have been studied quite extensively by Desfrançois *et al.*[14]

Almost all of these theoretical and experimental studies have dealt with closed-shell neutral molecules, for which the dipole-bound negative ion states are conceptually simple to understand and can also be treated rather straightforwardly with the available quantum chemical machinery.

The present work is intended to provide a theoretical appreciation of some properties of high-spin dipole-bound negative ion states, which have been described only very recently.[15–16] The somewhat unconventional diatomic molecules have been chosen for this purpose, since they all exhibit high-spin neutral ground states and, moreover, some of them possess large static dipole moments in various neutral electronic states. These are the prerequisites for the occurrence of dipole-bound high-spin anion states. The essential features of these states as well as the highly severe computational problems encountered in such investigations will be addressed in this work.

PROCEDURES FOR DIPOLE-BOUND STATE DESCRIPTION

Dipolar electron binding is associated with very small binding energies as well as with an enormous spatial extent of the attached electron. Therefore, it is imperative to employ highly diffuse gaussian basis functions to allow for a reasonable description of the loosely bound electron. We used the cc-VQZ basis sets, augmented by a set of six diffuse s and six diffuse p gaussians, located on the electropositive atom, as the standard basis set. Their exponents α were determined in an even-tempered fashion, according to $\alpha^l_{n+1} = \alpha^l_n \times \beta$ with $\beta = 0.316$, where α^l_0 corresponds to the most diffuse basis function for the angular momentum l. The most diffuse exponents created in this manner were 10^{-6}, which, in principle, facilitate a proper description of electrons residing in orbitals with a radial extent up to some 500 bohr.

Since the binding energy of the extra electron is small and its actual magnitude is essentially determined by electron correlation effects, it is indispensable to employ a theoretical approach that affords both size-consistency as well as recovery of a large portion of the valence correlation energy. MPn and CCSD(T) methodologies can both meet these requirements, and in fact they are frequently used for calculating dipolar binding to closed-shell molecules. The neutral ground states and the corresponding dipole-bound negative ion states possess disjunct spin multiplicities in these cases, and the desired dipole-bound state corresponds to the negative ion ground state. For this reason and because most of the neutral species investigated hitherto are well described by a single reference wavefunction, these two post-SCF methods have yielded meaningful results. For molecules such as CBe, SiBe, CMg, and SiMg, however, even the $^3\Sigma^-$ neutral ground states wavefunctions exhibit significant mixing of configurations, which advocates the usage of a multi-reference CI method. Moreover, there are valence- and dipole-bound anion states possessing the same symmetries, which inevitably leads to a state-averaging procedure. To overcome all these difficulties, we employed the MR-ACPF method, which is a size-consistent variety of a multi-reference CI procedure, in the MOLPRO[17] implementation.

On account of the extremely diffuse SOMOs of such dipole-bound anions, all integrals were calculated to a much higher than standard precision in order to avoid spurious results. Convergence thresholds for the energies were set at 10^{-10} for the same reason.

DISCUSSION OF DIPOLE-BOUND NEGATIVE ION STATES

The XY (X = C, Si; Y = Be, Mg) diatomics all have $^3\Sigma^-$ neutral ground states and the respective negative ion ground states belong to $^4\Sigma^-$.[15] CNa and SiNa own $^4\Sigma^-$ neutral ground states, whereas $^3\Sigma^-$ are the pertaining negative ion states. The most important data like electron affinities (EA), which correspond to $-T_0$, equilibrium distances, R_e, and dipole moments are compiled for all these species in Table I.

It can easily be recognized that the electron affinities, *i.e.* $-T_0$, of the XBe and XMg (X = C, Si) diatomics in their $^3\Sigma^-$ ground states are well over 1 eV and, thus, rather sizeable. Each of these anions possesses at least three stable excited states, in specific $^2\Pi$, $^2\Sigma^-$, and $^2\Delta$, which will not be dealt with

TABLE I

T_0 and R_e values and dipole moments of the neutral ground states and some negative ion states of CBe, SiBe, CMg, SiMg, CNa, and SiNa. Characterization of valence-bound (v) and dipole-bound (d) anion states is given in the third column. All data are taken from a previous work.[15,16]

System	State	Char.	T_0 / cm^{-1}	R_e / bohr	μ / D
CBe	$X^3\Sigma^-$	v	0	3.183	1.70
CBe$^-$	$X^4\Sigma^-$	v	–10908	3.238	3.98
CMg	$X^3\Sigma^-$	v	0	3.948	3.51
CMg$^-$	$X^4\Sigma^-$	v	–9489	4.165	1.56
SiBe	$X^3\Sigma^-$	v	0	4.035	1.63
SiBe$^-$	$X^4\Sigma^-$	v	–11509	4.107	1.91
SiMg	$X^3\Sigma^-$	v	0	4.823	3.48
SiMg$^-$	$X^4\Sigma^-$	v	–9961	5.038	0.98
SiMg$^-$	$1^4\Sigma^-$	d	–72	4.837	72.40
CNa	$X^4\Sigma^-$	v	0	4.283	8.12
CNa$^-$	$X^3\Sigma^-$	v	–5420	4.532	3.22
CNa$^-$	$1^3\Sigma^-$	d	–236	4.291	
CNa$^-$	$1^5\Sigma^-$	d	–217	4.299	
SiNa	$X^4\Sigma^-$	v	0	5.175	8.37
SiNa$^-$	$X^3\Sigma^-$	v	–7517	5.544	1.56
SiNa$^-$	$1^5\Sigma^-$	d	–246	5.195	
SiNa$^-$	$2^5\Sigma^-$	d	–118	4.177	

in this context. CBe and SiBe exhibit dipole moments of 1.70 and 1.60 D, respectively, which are too small to support a dipole-bound negative ion state. The dipole moments of CMg (3.51 D) and SiMg (3.48 D) are found to be significantly above the critical value, so both are candidates for dipolar electron binding.

Interestingly, the $1^4\Sigma^-$ dipolar state of CMg$^-$ is only bound for internuclear distances beyond R_e, whereas it lies higher in energy than the $^3\Sigma^-$ neutral ground state for $R < 4.0$ bohr. According to these results, this state is metastable and should exhibit a short lifetime, since both transition to the $X^4\Sigma^-$ state and electron autodetachment are allowed processes. Besides the $X^4\Sigma^-$ ground state, a stable dipole-bound ($1^4\Sigma^-$) negative ion state could be found for SiMg$^-$. The corresponding adiabatic electron affinity of 72 cm^{-1} ($\approx$ 9 meV) is quite small and in the expected range for a dipole moment of some 3.5 D. The actual calculations were performed in a state-averaged MR-ACPF fashion, giving equal weights to the valence- and dipolar $^4\Sigma^-$

states. Figure 1 displays the electron binding energy of the dipolar negative ion state with respect to the internuclear distance together with the dipole moment of the $^3\Sigma^-$ neutral ground state. The qualitative similarity of both curves is obvious, which corroborates the dipolar character of this state, in which the binding energy essentially follows the dipole moment. There is, however, a significant shift between the two curves, which becomes especially apparent by the non-coincident maxima. This is a consequence of electron repulsion and correlation effects, which modify the simple dipolar picture. It has to be noted that some 50% of the dipolar binding energy in the $1^3\Sigma^-$ state is accounted for by electron correlation, which is in line with the findings for other molecules.[18]

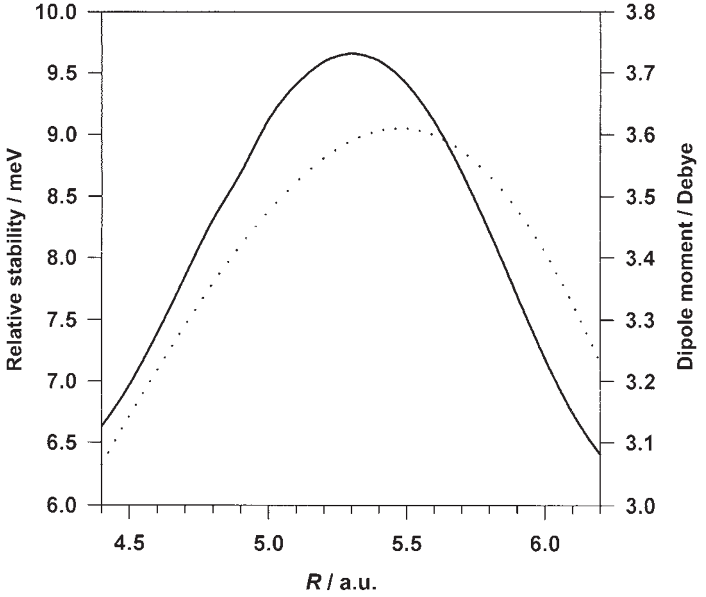

Figure 1. Dipole moment (dotted curve) of the $^3\Sigma^-$ ground state of SiMg and electron binding energy (solid curve) for the $1^4\Sigma^-$ dipole bound anion state of SiMg$^-$. Taken from reference 15.

Figure 2 presents a contour surface of the $1^4\Sigma^-$ SOMO orbital at the equilibrium distance, which can be considered as a paradigm of a dipole-bound electron. The center of charge is seen to be far off the molecule, beyond the magnesium atom, which constitutes the positive end of the dipole. This sketch reflects the enormous spatial extent of such dipole-bound electrons, which might be viewed as siblings of Rydberg states in a certain sense. Despite their common diffuseness, this analogy should not be taken

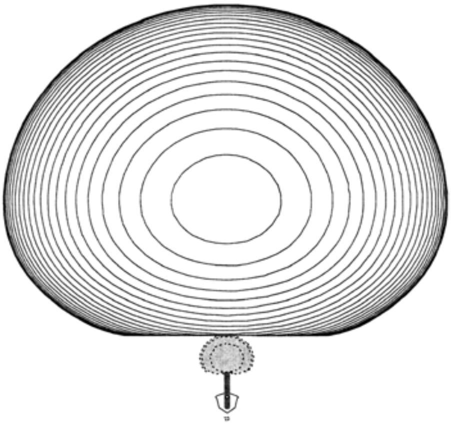

Figure 2. Contour surface (0.002) of the highest occupied orbital of the dipole-bound $1^4\Sigma^-$ state of $SiMg^-$. Taken from reference 15.

too seriously, since there are fundamental differences due to the different underlying physical mechanisms: The cation sits in the center of a Rydberg orbital, whereas the dipole-bound electron always resides preferentially beyond the positive dipolar end of the molecule. Core penetration is essential for Rydberg electrons but it can be rather small for dipole-bound electrons. Rydberg series constitute infinite manifolds of bound states, whereas only very few (mostly just one) dipole-bound anion states can be supported by a polar molecule. The latter can also easily undergo electron detachment by rotational excitation.

From Table I it may be seen that CNa and SiNa have even large dipole moments of some 8.4 D in their respective $^4\Sigma^-$ neutral ground states. In addition to their valence-bound $^3\Sigma^-$ and $^5\Sigma^-$ negative ion states, both molecules are expected to support dipole-bound anion states. On account of the large dipole moment, two dipole-bound $^5\Sigma^-$ could be found for $SiNa^-$, the binding energies of which are displayed in Figure 3. Akin to $SiMg^-$, it is seen that the binding energy in the more stable $1^5\Sigma^-$ state, which shows an adiabatic electron affinity of 246 cm^{-1}, essentially reflects the course of the dipole moment in the $^4\Sigma^-$ neutral parent state. The binding energy of the $2^5\Sigma^-$ state with an adiabatic electron affinity of 118 cm^{-1}, exhibits, however, no significant dependence on the dipole moment of the SiNa ground state. Both dipole-bound states become unstable and turn to continuum states for internuclear distances between 8.5 to 9 bohr. In this region, the curves should be taken just as an approximation, since the correct transmutation of a dipole-bound to a continuum state is highly complicated. The reason for this is on the one hand the finite basis set, which may fail for very small binding energies and on the other hand the invalidity of the Born-Oppenheimer ap-

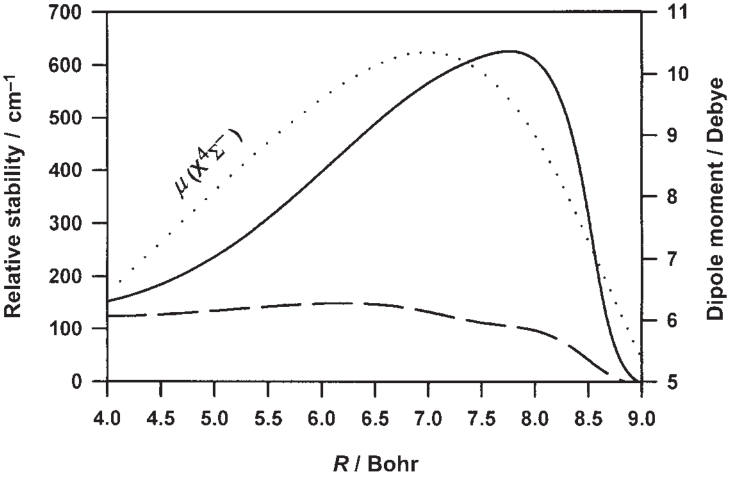

Figure 3. Dipole moment (dotted curve) of the $^4\Sigma^-$ ground state of SiNa and electron binding energies of the first $1^5\Sigma^-$ (solid curve) and the second $2^5\Sigma^-$ (dashed curve) dipole-bound state of SiNa$^-$. Taken from reference 16.

proach for binding energies on the order of the rotational constant B_e or less. Since the B_e-value is only some 0.4 cm^{-1} (Ref. 16) for SiNa, this may not lead to a serious deviation of the presented energy curves from the »exact« ones for $R > 8.5$ bohr.

The R_e values in Table I reveal that the geometries of the dipole-bound anions are rather similar to those of the corresponding neutral parent states. There are deviations of 0.015 bohr for SiMg$^-$, 0.02 bohr for $1^5\Sigma^-$ and 0.002 bohr for $2^5\Sigma^-$ states of SiNa$^-$.

Due to the loosely-bound character of the excess electron in the dipole-bound anions, spin-coupling with the neutral moiety is expected to have only a minor effect on the pertinent electron affinity. Therefore, two dipolar $^3\Sigma^-$ states are expected to exist in SiNa$^-$ as well. Unfortunately, severe numerical problems defeated the theoretical study of these states because, unlike $^5\Sigma^-$, the $X^3\Sigma^-$ state cannot be reasonably described with a single configuration. With the definition of the three configurations, $\Phi_1 = (1\sigma^+)^2\,(2\sigma^+)^2\,(1\pi)^2$, $\Phi_2 = (1\sigma^+)^2\,(3\sigma^+)^2\,(1\pi)^2$, and $\Phi_3 = (1\sigma^+)^2\,(2\sigma^+)\,(3\sigma^+)\,(1\pi)^2$ where the core is ignored and only the valence orbitals are counted, the MCSCF reference wave-function $\Psi(X^3\Sigma^-)$ of the $X^3\Sigma^-$ is obtained as $\Psi(X^3\Sigma^-) = 0.76\Phi_1 - 0.38\Phi_2 + 0.34\Phi_3$, which indicates a strong left-right correlation of the bonding $(2\sigma^+)$ orbital. Consequently, in state-averaged CASSCF calculations, the $(3\sigma^+)$ orbital is dominated by the electron correlation demands of the $(2\sigma^+)$ orbital rather than by the diffuse character of the dipole-bound electron. Thus, a delicate balance between diffuseness, as demanded by dipolar binding, and compactness, needed for efficient correlation, determines the characteristics of ($3\sigma^+$) and the next higher σ-orbitals. These may change significantly upon bond distortions and impair the overlap of reference and ACPF wavefunctions, which eventually thwarts the converged results. Some converged results for the first $^3\Sigma^-$ dipole-bound state could be achieved for $R > R_e$, where the corresponding binding energies were approximately 15–25 cm^{-1} lower compared to the respective $1^5\Sigma^-$ state. From this we can infer that the triplet-quintet splitting for the dipole-bound $SiNa^-$ states amounts to some 20 cm^{-1}.

For CNa^-, we succeeded in computing not only the dipole-bound $1^5\Sigma^-$ state but even the $1^3\Sigma^-$ state at least in the region 4.0 bohr $\leq R \leq$ 4.7 bohr around the equilibrium bond distance of the $X^3\Sigma^-$ neutral ground state. The adiabatic electron affinities are 236 and 217 cm^{-1}, respectively, for $1^3\Sigma^-$ and $1^5\Sigma^-$. This suggests a triplet-quintet splitting of 19 cm^{-1}, which is, in fact, quite small.

Since also the excited neutral states of SiNa possess dipole moments in the range of 6–8.2 D, it emerges that we should expect a pertinent dipole-bound negative ion state close to each neutral state. We tested this hypothesis for SiNa ($^2\Pi$), which has a dipole moment of 6.1 D. The corresponding $1^3\Pi$ dipolar anion state lies 3991 cm^{-1} higher in energy than the $X^3\Sigma^-$ ground state, but it exhibits an adiabatic stability of 52 cm^{-1} over its $^2\Pi$ neutral parent.

CONCLUDING REMARKS

Among the somewhat unconventional diatomics, consisting of a group 1 or 2 atom in conjunction with a group 14 atom, SiMg and SiNa are found to have $^3\Sigma^-$ and $^4\Sigma^-$ high-spin neutral ground states, respectively. The notable pertinent static dipole moments of 3.5 and 8.4 D, respectively, make them suitable candidates for the study of dipole-bound negative ions in high-spin states. While the ground state electron affinities for SiMg and SiNa amount to 9961 cm^{-1} and 7515 cm^{-1}, respectively, the adiabatic electron binding energies in the excited dipole-bound anion states are only 76 cm^{-1} ($1^4\Sigma^-$) and 243 cm^{-1} ($1^5\Sigma^-$). The binding energies of the lowest dipole-bound anion states, as functions of the internuclear distance, essentially reflect the dipole moments of the corresponding neutral ground states. Consequently, these states break down and become unbound at bond distances where the polarity of the neutral ground state diappears due to dissociation into the ground state atoms.

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SAŽETAK

Paradigme dipolno vezanih negativnih ionskih stanja u dvoatomnim molekulama visokoga spinskog multipliciteta

Josef Kalcher

Razmatrano je dipolno vezanje elektrona na dvoatomne molekule SiBe, SiMg, CNa i SiNa, koje imaju osnovna stanja visokih spinskih multipliciteta. Sve te molekule imaju jedno ili više valencijski pobuđenih anionskih stanja.