Mixed Valence Character of Anionic Linear Beryllium Chains: A CAS-SCF and MR-CI Study[†]

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A theoretical investigation on the mixed valence behavior, or bistability, of a series of anionic linear chains composed of beryllium atoms is presented. Calculations on Be_N^- (with $N = 7, ..., 13$) were performed at CAS-SCF and MR-CI levels by using an ANO basis set containing 6s4p3d2f contracted orbitals for each atom. Our results show a consistent gradual shift between different classes of mixed valence compounds as the number of beryllium atoms increases, from strong coupling (class III) toward valence-trapped (class II). Indeed, in the largest cases ($N > 10$), the anionic chains were found to become asymptotically closer to class I, where the coupling vanishes. The intramolecular electron-transfer parameters V_{ab}, E_{barr}, and E_{opt} were calculated for each atomic chain. It is shown that the decrease of V_{ab} with increasing N follows an exponential pattern.

1. Introduction

Due to the relevance of the electron-transfer (ET) reactions in many biological and chemical systems, the deep understanding of the key parameters governing the ET processes, aimed at their full control, has attracted great interest in the last decades.[1] A mixed valence (MV) system consists of two redox centers, usually linked through a bridge, which act, respectively, as an electron donor (D) and acceptor (A); the ET reaction from D to A can be induced by either thermal activation or optical excitation. MV molecules are extensively studied for their optical and magnetic properties as well as for their application in molecular electronics and photonics[2] since their appealing future is the possibility of modeling the optical properties through the control of the parameters influencing the rate of the ET reaction.[3,4] To this aim, the electronic coupling between the two redox centers plays the major role in governing the ET rate. The coupling is given by $\mathscr{H}_{\mathrm{AB}} = \langle\psi_{\mathrm{A}}|\mathscr{H}|\psi_{\mathrm{B}}\rangle$, where Ψ_{A} and Ψ_{B} localized states where the charge (or hole, depending on the type of ET process) is placed on site A or B, respectively. On the basis of the Robin and Day classification,[3] MV systems are commonly subdivided into three categories, depending on the relationship between the electronic coupling and the thermal activation energy. The classification goes from essentially zero electronic coupling (class I), to medium coupling (class II), to strong coupling (class III). Obviously, the most interesting molecules are those belonging to the class II (valence trapping) and class III (delocalized valency) categories and, particularly, the borderline compounds between class II and class III.[5–9] The peculiarity of these compounds is the presence in the near-infrared (NIR) of a characteristic absorption band (intravalence (IV) CT band), arising from the optical excitation from the minimum of the ground state to the lowest excited state. Generally, if no strong vibronic couplings occur and the IV band has a rather symmetric shape, a simple semiclassical approach[4–10] can already provide all of the relevant ET parameters, such as the electronic coupling and the reorganization energy λ (or E_{opt}) (see Figure 1). However, in the case of strongly coupled systems, for which the simple Hush's approach[4,10] generally fails, the use of more rigorous quantum mechanic methodologies becomes necessary. The simplest approach to describe the ET in a MV system is to use a Marcus-like two-state one-mode model, where for a symmetric MV system (Figure 1), the electronic coupling $\mathscr{H}_{\mathrm{AB}}$ is given by half of the energy splitting (V_{ab}) between the two adiabatic potential surfaces at the crossing seam and the reorganization energy, λ, is computed as the vertical excitation energy from the localized minimum of the ground state to the first excited state.[11–18] This simple relation is justified since we are dealing with a symmetric mixed valence compound; in the most general case, the reorganization energy should be considered as the Gibbs free energy dissipated when the system relaxes

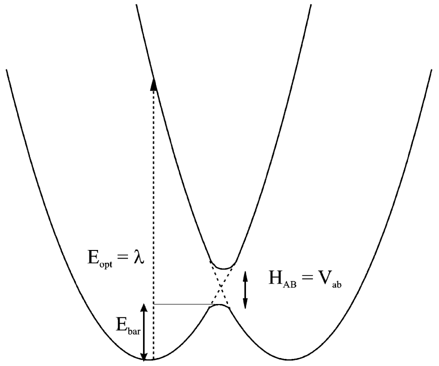

Figure 1. Potential energy surfaces of an electron-transfer reaction in a symmetric MV class II compound.

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to a new charge-localized equilibrium state after a vertical excitation from the other minimum.

On the basis of our previous experience on both MV systems[16–19] and atomic metallic chains,[19–24] in the present contribution, we propose a systematic variational study on the MV character of anionic linear beryllium chains. Due to the recent advances in the experimental techniques, which have made possible the precise deposition of atomic metallic chains on surfaces of nanometer scale,[25–28] the research interest for this kind of systems has rapidly grown. As it has been shown and discussed,[20,21] the interesting characteristic of these atomic linear beryllium chains is the formation of edge orbitals localized at the two extremities, which gives rise to two quasi-degenerate electronic states, namely, an open-shell $^1\Sigma_g^+$ singlet and a $^3\Sigma_u^+$ triplet. As the length of the chain increases (i.e., the value of N increases), the quasi-degeneration between the edge orbitals also increase, removing the singlet–triplet energy splitting. Indeed, the antiferromagnetic coupling between singlet and triplet states decays exponentially with N. Furthermore, as we have widely discussed,[20–22] the theoretical description of these atomic chains turns out to be rather problematic because of the completely different electronic configuration of the system near the equilibrium distance and when approaching the dissociation. In fact, while for a Be_N chain near the energy minimum $2N - 2$ electrons occupy the $N - 1$ inner orbitals and the remaining two electrons half-fill each of the two edge-orbitals, at larger distances, the orbitals are essentially a linear combination of s orbitals of noninteracting Be atoms. It is, however, important to remind that linear geometry represents a local minimum on the potential energy surface for such systems.[23] A mixed valence behavior has been evidenced for the cations[19] with the charge ("hole" in this case) deplacing from one edge orbital to the other and with the adiabatic coupling governing the process following an exponential law with respect to the value of N. Therefore, all of the three classes of mixed valence compounds can be obtained simply by varying the length of the chain. Following our previous work on cationic chains,[19] we present here the results of a complete active space self-consistent field (CAS-SCF) and contracted multireference configuration interaction (C_MR-CI)[29,30] study of the ET process along a simplified reaction coordinate (see ref 16 for a more detailed discussion). The present paper is organized as follows. In section 2, computational details are presented; in section 3, FCI benchmarks on electron affinity are reported and the stability of anionic chains is discussed; finally, results are discussed in section 4, and conclusions are drawn in section 5.

2. Computational Details

All the CAS-SCF and C_MR-CI computations for the anionic chains (from Be_7 to Be_{13}) have been carried out with an ANO-L type basis set.[32] The contraction 6s4p3d2f was adopted, and the calculations were performed by using the MOLPRO2.6 package.[31] As MOLPRO can only treat Abelian point groups, all calculations of the geometry optimizations and of the potential energy surfaces (PESs) have been performed using the reduced C_{2v} symmetry.

Following the strategy of our previous works on mixed valence systems,[16–19] the ET was studied along an approximate reaction path, obtained by the linear mixing of the Cartesian coordinates of the two charge-localized C_{2v} geometries

$$Q(\xi) = \left(\frac{1}{2} - \xi\right)Q_\mathrm{A} + \left(\frac{1}{2} + \xi\right)Q_\mathrm{B} \qquad (1)$$

where Q_A and Q_B are the coordinates of the two distorted equivalent minima. The distorted C_{2v} geometries of the anion Be_7^-–Be_{13}^- chains were obtained by optimizing the system at the CAS-SCF level with the above-cited basis set. The active space chosen for the geometry optimizations was composed of three electrons in four orbitals, CAS(3/4):

- The two edge orbitals. They belong to the σ_g and σ_u irreps in $D_{\infty h}$ but merge into the a_1 irrep in the C_{2v} point group.
- Two π orbitals (one π_x and one π_y), of essentially p atomic character. These orbitals locate on the anionic Be atom at one extremity of the chain and account for the large dynamic correlation due to the extra electron.

For the calculations of the PESs at CAS-SCF and MR-CI levels, a larger active space was adopted, including two more π orbitals. These extra orbitals are needed to obtain a balanced description of the moving electron from one edge of the chain to the other one. The four π have essentially p atomic character and spontaneously localize on the terminal Be atoms for all of the values of ξ, except for values close to zero (the avoided-crossing region); in this case, the π orbitals are a combination of the p orbitals of the two terminal Be atoms. The final active space was therefore composed of three electrons in six orbitals, CAS(3/6). To avoid PES discontinuities at the symmetrical saddle point, state-averaged CAS-SCF optimizations over the two $^2\mathrm{A}_1$ states involved in the ET were performed. The mixing parameter ξ was varied, in steps of 0.05, from -1.50 to $+1.50$. Notice that, with the notation adopted in eq 1, the saddle point corresponds to the value $\xi = 0$, while the two distorted minima correspondto the values of $\xi = +1/2$ and $-1/2$. Finally, all FCI computations have been performed by using the Bologna code.[33,34] Molecular orbital integrals were computed by using the Dalton 2.0 suite,[35] while codes were interfaced by using the newly developed Q5Cost format and libraries.[36–40]

3. Anionic Chain Stability

Before describing the mixed valence behavior of anionic beryllium chains, it is important to analyze the problem of the stability of the anionic species with respect to the neutral systems. Indeed, at CAS-SCF and MR-CI levels, the neutral chains lie below the anionic systems for all of the points of the reaction coordinate. This fact might suggest that the Be_N^- chains could be unstable with respect to the neutral ones. For those reasons, we performed full configuration interactions (FCI) computations on some selected systems to asses if this phenomenon has to be ascribed to an underestimation of the Be_N^- energy and thus of the electron affinity. All of the FCI computations have been computed on chains in which the constituent atoms have been kept fixed at a distance of 4.25 bohr, this geometry being quite close to the equilibrium for all of the neutral chains.[20–22] Therefore, since at the FCI level we did not optimize the charged systems, the computed electron affinities represent a lower bound. Due to the huge computational cost of FCI computations, we limited the study to a representative subsystem, investigating the combined effect of the basis set and the length of the chains. In particular, we performed FCI for the Be_2 and Be_2^- systems using 3s1p, 4s2p, 4s2p1d, and 5s3p2d ANO-L basis. By using the 3s1p basis, we performed FCI on chains composed of 2, 3, 4, and 5 atoms, respectively. FCI results are collected in Table 1. In particular, one can see that the augmentation of the basis size leads to an increase of the electron affinities. By using the 5s3p2d basis set, a stable Be_2^- is predicted. With the smallest 3s1p basis set, we performed FCI up to $N = 5$ (in this case, we had to deal with a FCI space of about 1.2×10^9 symmetry-adapted

TABLE 1: FCI Electron Affinities (in hartrees) for Be_2 with Various Basis Sets and Be_N Chains with a 3s1p Basis Set[a]

basis	EA
3s1p	−0.034647
4s2p	−0.014917
4s2p1d	0.001652
5s3p2d	0.007715

N	EA (3s1p basis)
3	−0.046150
4	−0.046052
5	−0.012544

[a] Be−Be distance fixed at 4.25 bohr.

TABLE 2: Bond Lengths (bohr) of the Optimized Localized Be_N^- Chains[a]

	bond length						
bond	$N = 7$	$N = 8$	$N = 9$	$N = 10$	$N = 11$	$N = 12$	$N = 13$
1−2	4.3505	4.3513	4.3506	4.3500	4.3498	4.3496	4.3493
2−3	4.1156	4.2262	4.2265	4.2255	4.2263	4.2262	4.2263
3−4	4.1589	4.1601	4.1608	4.1611	4.1616	4.1613	4.1614
4−5	4.1333	4.1364	4.1380	4.1386	4.1393	4.1393	4.1394
5−6	4.1157	4.1226	4.1259	4.1277	4.1285	4.1288	4.1290
6−7	4.1251	4.1101	4.1173	4.1209	4.1226	4.1234	4.1236
7−8		4.1205	4.1069	4.1145	4.1180	4.1198	4.1205
8−9			4.1178	4.1050	4.1127	4.1164	4.1181
9−10				4.1162	4.1040	4.1117	4.1153
10−11					4.1147	4.1031	4.1110
11−12						4.1142	4.1026
12−13							4.1136

[a] For convention, the bonds are numbered starting from the Be atoms bearing the negative charge (1−2).

determinants). It is noteworthy to see that by augmenting the chain length from $N = 3$ to 5, the stability of the neutral chain is significantly decreased. These results confirm our hypothesis on the stability of the anionic chains and, since the electron affinity increases with N, support the decision to study the bistability of medium-long chains.

4. Results and Discussion

The bond lengths of the optimized Be_N^- geometries are presented in Table 2. Due to the chosen active space, the deformed, or charge-localized geometry, is favored in the geometry optimization even for shorter chains. Therefore, we should refer to the results in Table 2 as optimized localized bond lengths. The bond numbering scheme can be summarized as follows: bond number 1 is the terminal bond on the "anionic" side, that is, the side where the charge is localized, bond 2 is the bond adjacent to bond 1, and so forth. In this way, the last bond for each chain (bond $N - 1$) is the terminal bond on the "neutral" side. When looking at the bond lengths of Be_N^- collected in Table 2, one can immediately notice the strong geometry deformation of all of the beryllium chains and, therefore, the strong localization of the negative charge in a terminal bond of a chain. For instance, the terminal "anionic" bond for $N = 7$ is 4.3505 bohr, while the internal bonds are significantly shorter, their values ranging from 4.1156 to 4.1589 bohr. A similar behavior was already present on the cationic chains.[19] A further analogy with the results reported in ref 19 is the behavior of the single bond lengths with N. It is worthwhile to note that, excluding $N = 7$, bond 2−3 is slightly more "anionic", that is, longer, than bonds number 3−4 to $(N - 1)-N$ but significantly less than bond 1−2. It is also interesting to note that the deformation of bond 1−2 is almost constant upon varying N. As an example, we can see that the bond length is 4.3513 bohr for $N = 7$ and 4.3493 bohr for $N = 13$. Similar behaviors can be found for the other bonds.

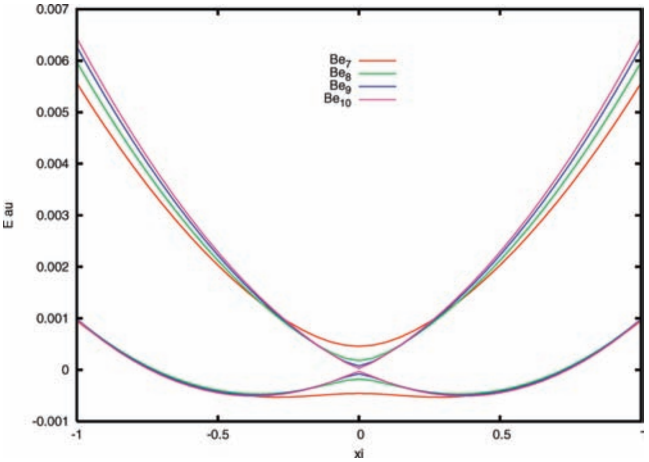

Figure 2. CAS-SCF PESs of Be_N^- chains against the geometrical deformation parameter ξ. Energy in hartrees.

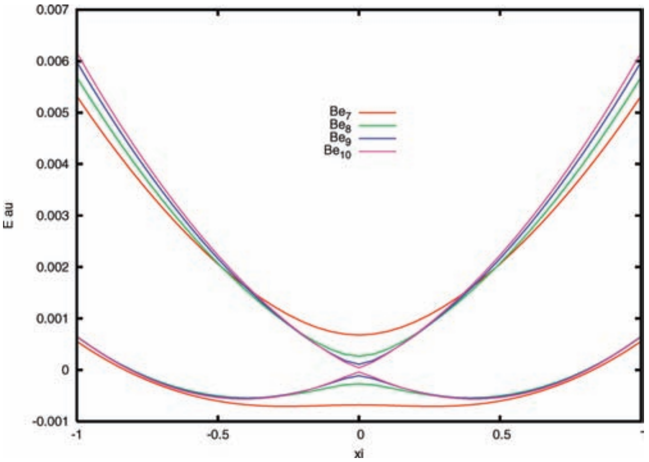

Figure 3. MR-CI PESs of Be_N^- chains against the geometrical deformation parameter ξ. Energy in hartrees.

CAS-SCF and MR-CI PESs as a function of ξ for Be_N^- are shown in Figures 2 and 3, respectively. The figures show PESs for $N = 7-10$. These plots represent the adiabatic surfaces of the Be_N^- chains, where, for each chain, the lowest electronic ground state is the 1^2A_1 state by using the corresponding C_{2v} symmetry elements and the first excited electronic state is the 2^2A_1 state. The absolute atomic unit energies of all of the electronic states were opportunely scaled in order to set the zero of the energy scale to the middle point of the splitting between the ground and first excited states at the crossing seam, $\xi = 0$. The values of V_{ab}, E_{barr}, and E_{opt} for Be_N^- chains using CAS-SCF and MR-CI are presented in Table 3. In particular, E_{opt} has been computed as the vertical excitation energy at $|\xi| = 0.5$

A consistent gradual shift toward valence trapping, or bistability, from $N = 7$ to 13 is observed. The Be_N^- chains tend to move from class III to class I (asymptotically), passing by class II, mixed valence systems, by increasing the number of beryllium atoms N in a chain. This is true for both CAS-SCF and MR-CI calculations, as shown in Figures 2 and 3, although the bistability is more pronounced at the CAS-SCF level. For instance, for $N = 7$, a very weak valence trapping, or charge localization, is observed since the values of V_{ab} are relatively

TABLE 3: CAS-SCF and MR-CI ET Parameters (kJ/mol) for the Be_N^- Chains[a]

method	energy	$N = 7$	$N = 8$	$N = 9$	$N = 10$	$N = 11$	$N = 12$	$N = 13$
CAS-SCF	V_{ab}	2.399	0.940	0.394	0.144	0.068	0.019	0.015
	E_{barr}	−0.115	0.567	0.914	1.106	1.191	1.253	1.280
	E_{opt}	6.417	6.609	6.953	7.186	7.395	7.515	7.609
MR-CI	V_{ab}	3.567	1.408	0.584	0.216	0.098	0.029	0.020
	E_{barr}	−0.199	0.617	1.066	1.302	1.401	1.465	1.517
	E_{opt}	6.997	6.764	7.041	7.260	7.465	7.583	7.674

[a] The energy splitting at the crossing seam (V_{ab}), the height of the barrier for the thermal ET (E_{barr}), and the excitation energy corresponding to the optical ET activation are reported.

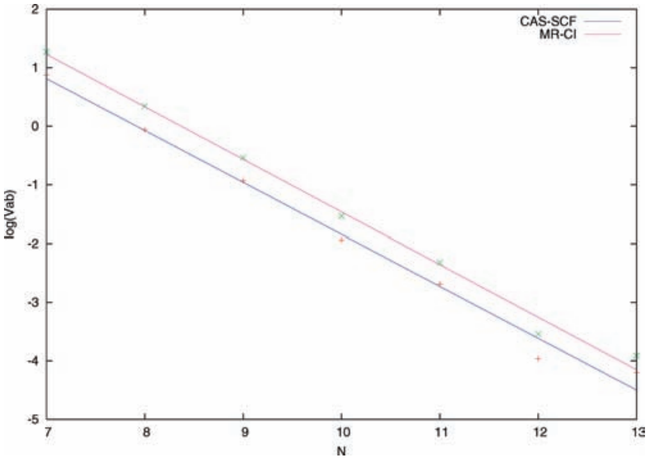

Figure 4. V_{ab} versus N plotted on a logarhitmic scale.

large and that of E_{barr} are very small On the other hand, beryllium chains with far higher N, say 10−13, have relatively high energy barrier E_{barr} values and relatively low electronic coupling $2V_{ab}$ values; see Table 3. Note that in the case of the shortest chains, a negative activation energy (single well energy curve) is obtained, although geometry optimization in Table 2 shows a distortion coherent with a charge localization. As stated previously, this is due to the fact that optimizations have been carried on by using a state-specific CAS-SCF wave function with a small active space, therefore favoring the charge-localized state.

The MR-CI results, when compared with that of CAS-SCF, tend to slightly increase the energy separation between the adiabatic ground state, 1^2A_1, and the first excited electronic state 2^2A_1 ($2V_{ab}$) for each N, as shown in Table 3, again a pattern coherent with results reported in.[19] As far as the activation energy E_{barr}, and the optical excitation E_{opt} are concerned, the MR-CI tends to increase the value of these parameters. These results are opposed to the ones observed for cationic chains in which the inclusion of the dynamical correlation produced a decrease of the E_{barr} value.

The relationship between the coupling V_{ab} and the number of beryllium atoms N in a chain has been considered. The two quantities obey to an exponential relationship

$$V_{ab}(N) = V_{ab}^0 e^{-\alpha N} \qquad (2)$$

where V_{ab}^0 is a constant. A plot of log V_{ab} as a function of N is shown in Figure 4. An overall linear behavior is observed, confirming the previous relationship. However, slight deviations from linearity appear for the highest N values, again, a pattern already evidenced on cationic chains. The same behavior was also obtained at the MR-CI level. A least-squares fitting has been performed on log V_{ab} and reported in Figure 4. This procedure gives a value of the slope α of 0.885 for the CAS-SCF computations and of 0.896 for the MR-CI ones. The fitted log V_{ab}^0 values, on the other hand, are 7.008 and 7.503 for the CAS-SCF and MR-CI, respectively.

The simplest model of MV systems is obtained if two states interact through a perturbation described by a constant coupling. Usually, the energy of the unperturbed states is assumed to have a parabolic shape as a function of the geometrical distortion. The previously studied cations were found to follow very well this naive picture, with parabolic energies independent from the length of the chain and a coupling constant quickly decreasing with N. In the present case of anionic chains, on the other hand, the agreement is much worse, as one can see in Figures 2 and 3. Indeed, the curves corresponding to different values of N cross for $|\xi| \simeq 0.4$ (excited states) and 0.8 (ground states), and this is clearly not consistent with the simple model of two parabolas interacting through a constant.

The present results confirm the possibility already shown in the case of the cations, to use anionic linear chains of beryllium atoms as electronic "charge-transfer" devices, in which intramolecular charge-transfer parameters, for example, V_{ab}, could be directly controlled, or "designed", by varying the number of atoms of the chain, even if the MV parameters computed for the anionic systems show a less pronounced mixed valence character with respect to the corresponding cations. As an example, the V_{ab} coupling constant is significantly lower for the anion. The ratio between the cationic and anionic coupling parameters is ∼4 for various chains lengths.

5. Conclusions

It has been shown that anionic linear beryllium chains behave like mixed valence systems when one electron is added to the system. An increase of mixed valence character (bistability or charge localization) with an increasing number of beryllium atoms N in an anionic chain has been evidenced. As expected in the case of extended mixed valence systems, there is a decreasing V_{ab} with increasing N. In particular, a linear relationship between log V_{ab} and the number of beryllium atoms (N) has been found. Indeed, at the equilibrium geometry, the chain length is, to a very good extent, directly proportional to the number of atoms. This fact justifies the exponential relationship between V_{ab} and the chain length, consistent with the fact that in the ion, the hole is located in one of the two edge orbitals.

These results are particularly interesting for at least two reasons. First of all, mixed valence systems could be used in order to design interesting devices, particularly in the field of Molecular Electronics. A promising possibility would be to deposit beryllium chains on nanodevices (on top of graphene surfaces and nanorods or inside of nanotubes) in order to exploit the mixed valence nature of the ions. The possibility of going from class I to class III in a tunable way, by simply changing the number of atoms in the chain, makes these systems particularly attractive. Moreover, as isolated objects, beryllium chains are relatively simple systems. For this reason, they are particularly suitable to assess the quality of the theoretical methods used to perform these studies. Finally, it is worth mentioning that preliminary investigations on neutral atomic chains containing atoms of the Groups 2 and 12 seem to indicate that the presence of edge orbitals is not restricted to beryllium alone. If these results were confirmed by subsequent investigations, the number of possibilities for mixed valence atomic chains would be extremely large. Although the stability of isolated chains toward collapse into more stable compact clusters is still to be investigated, linear structures could perhaps be stabilized by deposition on inert surfaces. This possibility, combined with the remarkable predicted properties of the neutral chains, could open interesting perspectives in the fast-growing field of nanodevices.

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