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Does a Sodium Atom Bind to C₆₀?

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Abstract: A Multi-Reference Configuration-Interaction study of the NaC₆₀ system is presented. It is shown that the experimentally measured dipole moment of this system can be explained by the existence of a charge-transfer state of Na⁺C₆₀[−] nature. Moreover, the present work shows that Configuration-Interaction techniques based on local orbitals permit a Multi-Reference treatment of systems containing several tens of atoms.

The interaction of fullerenes with alkaline atoms deserved a special attention in the past decade.^{1–5} In the case of sodium, a state with a dipole moment of 16.3 D has been detected for the NaC₆₀ system.^{6,7} Theoretical calculations predict a minimum for the sodium atom approaching one of the hexagonal faces of the fullerene.^{8,9} However, Unrestricted Hartree–Fock (UHF) and Density-Functional Theory (DFT) calculations give rather different values for the binding energy *D*: the system is virtually unbound at the UHF level¹⁰ (*D*=0.10 eV), while DFT-LDA gives a much larger value¹¹ (*D*=2.10 eV). The DFT-B3LYP result is placed between these two extrema⁸ (*D*=0.65 eV). The distance values between Na and the closest carbon atoms are close at the DFT level (2.69 Å for LDA and 2.74 Å for B3LYP), while UHF gives a very different result (5.08 Å). The fullerene π system is mainly concentrated on the hexagon bonds. For this reason, although the predicted energy difference between the hexagon site and the other positions is very small, it seems likely that the hexagon sites play a special role among the different adsorption positions.

If one neglects a possible Jahn–Teller distortion, the system has a C_{3v} symmetry in the case of a hexagon-approach path. In this case, three different states are in competition: (1) a neutral ²A₁ state, C₆₀ + Na, which is essentially *repulsive* (except for a possible van der Waals minimum at

large distance) and (2) a ionic ²E (doubly degenerated) state, C₆₀[−] + Na⁺, which is *attractive*.

To treat all these states on an equal foot, a Multi-Reference (MR) approach is strongly recommended. We used our recently developed local CAS-SCF formalism,^{12,13} which is able to concentrate the active space in the region of interest of a molecular system. According to our approach,^{14,15} we used a *minimal* active space at the CAS-SCF level, while the effect of dynamical correlation is included via a subsequent Configuration-Interaction (CI) treatment. For the present case, the active space is composed of three orbitals: the 3s sodium orbital (3s(Na)) and the two degenerated π^* orbitals which are delocalized on the hexagonal ring ($\pi_{\text{hex}}^*(\text{C}_{60})$).

Even with a small active space, the local MR-CI treatment on such a large system is extremely heavy. A possibility to reduce the size of the problem is to freeze some orbitals whose effect on the studied properties is expected to be small. For this reason, taking benefit of the use of localized orbitals, we froze most of the σ orbitals at the SCF level. Only the σ and σ^* orbitals nearest to Na (12 bonds, i.e., 24 orbitals) were correlated at the CI level.

The choice of the atomic basis set is a very sensible point. It is clear that a minimal basis set alone has not enough flexibility to describe the orbital relaxation and the correlation effects of this system. In particular, because of the competition between neutral and charged forms, the experimental ionization potential (IP) of Na and the electron affinity (EA) of C₆₀ must be accurately reproduced. Even with a minimal basis set, this is not a problem for Na (with the (3s2p) basis

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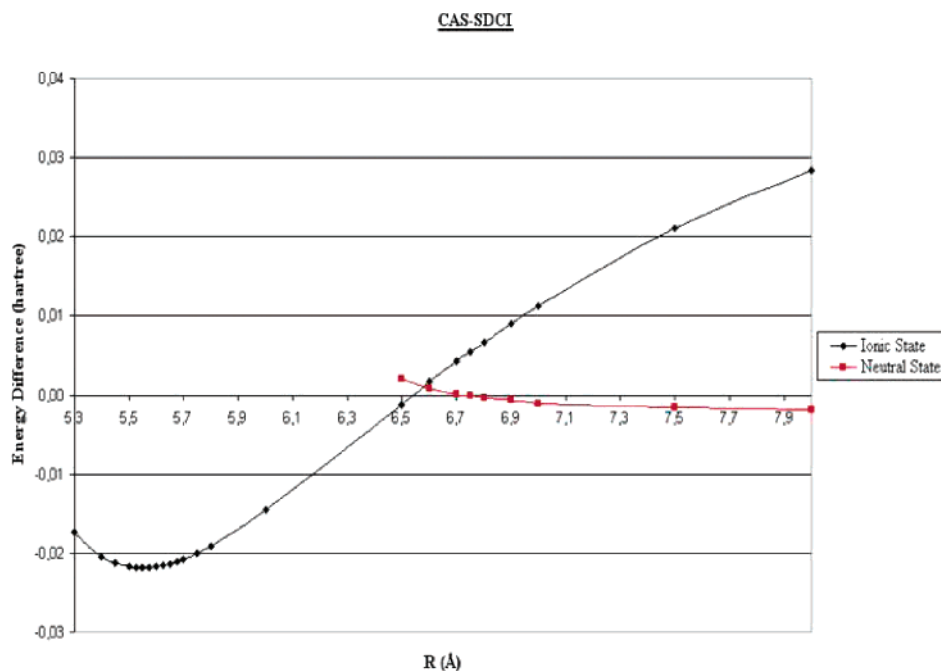


Figure 1. Energy curves of the 2A_1 and 2E states as a function of the distance between the Na atom and the C_{60} center. The energy zero corresponds to the value of the neutral 2A_1 state at infinite distance.

we obtain 4.90 eV to be compared with the experimental IP of about 5.14 eV). On the other hand, the minimal basis set is certainly too poor for C_{60} , since it leads to an $EA = 4.10$ eV, while the experimental value is substantially lower ($EA_{\text{exp}} = 2.65$ eV).

Therefore, to keep the basis-set size reasonable, we used an ANO (2s1p) basis on each carbon and a (3s2p) basis on the sodium atom,¹⁶ supplemented with a set of uncontracted Gaussians centered on the C_{60} center. We used a (1s1p1d1f1g1h1i) set of 49 functions, having a mean radius $\langle r \rangle$ equal to the C_{60} radius. These additional orbitals are intended to provide the required angular correlation to the mobile π electrons on the C_{60} surface. With this choice of the basis set, one has $EA = 2.28$ eV for C_{60} , in a reasonable accord with the experimental value. Therefore, this was our final basis-set choice.¹⁷

The MR-CI results (single and double excitations on the local CAS-SCF wave function) are reported in Figure 1. The neutral A_1 state is the lowest one at an infinite distance at the MR-CI level, and the ionic E state lies about 2.6 eV above the A_1 one at dissociation and becomes the lowest one at about $R = 6.5$ Å. At about $R = 5.55$ Å the E state has a minimum, 0.59 eV below the asymptotic energy of the A_1 state (see Table 1, E_D). The dipole moment (15.6 D) is in a good agreement with the experimental value of 16.3 D.^{6,7} The MR-CI results have been also corrected by using the Counter-Poise (CP) procedure,¹⁸ to take into account the Basis-Set Superposition Error (BSSE) (see Figure 2). The ionic minimum becomes less deep, and it is almost degenerated with the asymptotic energy of the neutral state at dissociation. The neutral state is less affected by the correction (that comes essentially from the effect of the sodium basis set on C_{60}^-), and a significant barrier separates the two minima (see Table 1, E_B). On the other hand, the

Table 1. MR-CI Results (with and without BSSE Correction) and Experimental Dipole Moment

| | R_e^a (Å) | E_D^b (eV) | E_B^c (eV) | μ^d (D) |
|--------------------------|-------------|--------------|--------------|-------------|
| NaC_{60} | 5.55 | 0.59 | 0.61 | 15.6 |
| $NaC_{60} + \text{BSSE}$ | 5.68 | 0.02 | 0.37 | 16.5 |
| experiment | | | | 16.3 |

^a R_e , equilibrium distance between the sodium atom and the center of C_{60} . The distances between Na and the closest C atoms are 2.72 and 2.83 Å (without and with BSSE correction, respectively) in good accord with the DFT values. ^b E_D , binding energy with respect to the neutral system at infinite distance. ^c E_B , dissociation barrier with respect to the ionic-state minimum. ^d μ , dipole moment.

position of the minimum and the corresponding value of the dipole moment are very little affected by the BSSE.

The small energy difference between the ionic minimum and the neutral asymptote raises the question of the stability of the ionic form. Since entropy favors the dissociated species, one can expect that, at thermodynamic equilibrium, the neutral form should dominate. However, the barrier to dissociation of the ionic species is not negligible. If the ionic curve is fitted with a Morse potential, the lowest vibrational level is only 237.3 cm^{-1} higher than the Morse ionic minimum, and about 20 vibrational levels are predicted below the barrier to dissociation ($E_B = 0.37$ eV with BSSE, see Table 1). For these reasons, one can expect the ionic minimum to have (at least) a metastable character.

It should also be noticed that several effects are expected to contribute to an ionic-minimum stabilization. One is geometry relaxation, including a symmetry lowering due to a Jahn–Teller effect. Moreover, the BSSE is often overestimated by the CP correction. Finally, the difference between the ionic and neutral asymptotes is $4.90 - 2.28 = 2.62$ eV with our calculations, while the experimental value is $5.14 - 2.65 = 2.49$ eV.

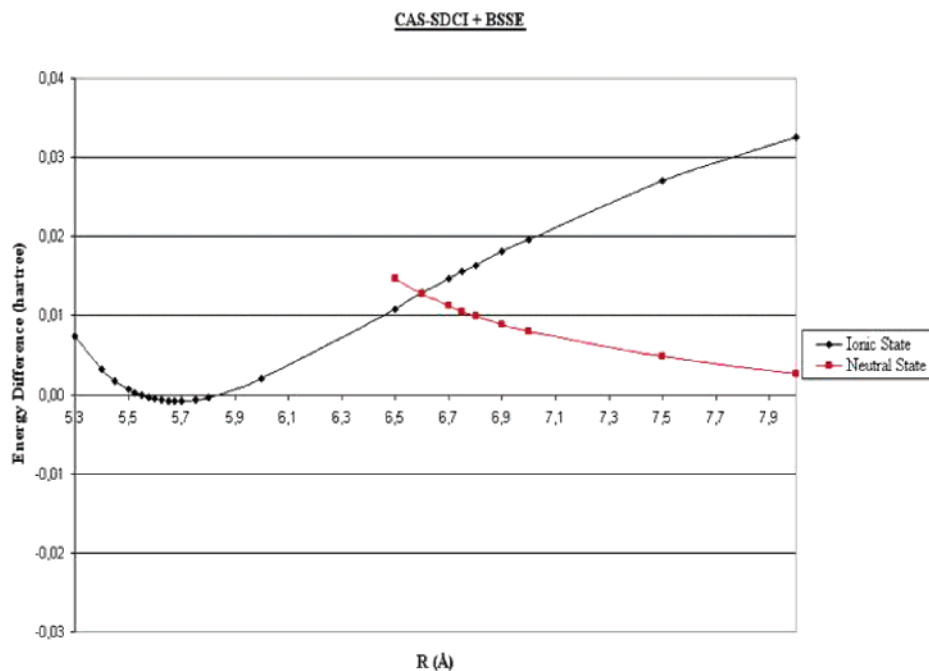


Figure 2. Same as Figure 1, with the inclusion of the BSSE correction.

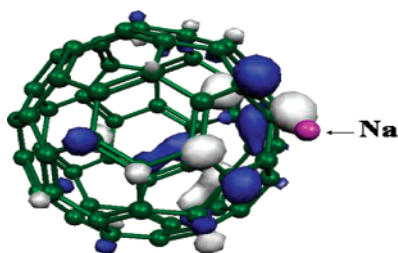


Figure 3. One of the active π^* orbitals of e symmetry, computed at the equilibrium distance of the ionic state.

In any case, our MR-CI calculations clearly indicate the presence of an ionic local minimum, having a dipole moment in excellent agreement with the experimental results. It seems likely to associate this local minimum (either an absolute one or a metastable minimum having a significant barrier to dissociation) to the experimentally detected species.

It is instructive to plot the active orbitals obtained through our local CAS-SCF algorithm. At the equilibrium distance of the attractive E state, the two π^* CAS-SCF orbitals are localized on the hexagon near to the sodium atom but show significant tails on the closest carbon atoms. This partially local behavior that was observed in local CAS-SCF treatment of other systems^{19,20} is due to the effect of the charged Na⁺ ion on the π^* electron, that cannot freely delocalize on the whole fullerene. One of the two degenerated π^* orbitals is shown in Figure 3.

In conclusion, the present study shows the existence of a charge-transfer local minimum on the Na + C₆₀ PES. The recently observed dipole moment of this system can be interpreted as due to this state, although further investigations are needed in order to discriminate between a global minimum and a meta-stable state having a significant barrier to dissociation. As a more general conclusion, the present work proves that local-orbital techniques permit a MR-CI

treatment of systems as large as a fullerene. These techniques can be a useful tool for those cases where several electronic states are in competition and for which DFT still presents open problems.

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