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A theoretical study of electronic spectra in the linear cationic chains $NC_{2n+1}N^+(n = 1–6)$

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ABSTRACT

The B3LYP, CAM-B3LYP, and RCCSD(T) theories have been used to calculate the ground state equilibrium geometries of the linear cationic chains $NC_{2n+1}N^+$ ($n = 1–6$). Compared with the system $NC_{2n}N^+$, the odd-n cationic chains are more susceptible to fragmentation than the even-n cationic chains. The complete active space self-consistent-field method has been utilized to determine the stationary structure of the ground state ($X^2\Pi_{g/u}$) and first excited state ($1^2\Pi_{u/g}$). The complete active space second-order perturbation theory has been used to compute the vertical excitation energies for the dipole-allowed $(1, 2, 3)^2\Pi_{u/g} \leftarrow X^2\Pi_{g/u}$ transitions as well as the dipole-forbidden $1^2\Phi_{u/g} \leftarrow X^2\Pi_{g/u}$ transitions. The calculated transition energies of $1^2\Pi_{u/g} \leftarrow X^2\Pi_{g/u}$ in the gas phase are 2.61, 2.37, 2.07, 1.88, 1.64, and 1.34 eV, respectively, which accord well with the available experimental values. Moreover, the absorption spectra of $2^2\Pi_{u/g} \leftarrow X^2\Pi_{g/u}$ may be detected more easily among the selected four transitions.

1. Introduction

As the important position of the pure carbon clusters in comets [1], interstellar molecular clouds [2,3], and chemical process [4,5], there has been a growing interest in the investigation of their structural and spectral properties [6–8]. For their high chemical activity, they can react with a wide variety of atoms facilely, forming even–odd systems of the type XC_nX or HC_nX (X = H, N, O, B, Al, S, Si·) [9]. Since the presence of such elements in carbon chains, their electronic and structural nature may be significantly modified.

In recent years, the linear carbon chains terminated by hydrogen atom or CN group are regarded as potential molecules in interstellar clouds and atmospheres of carbon stars [10] and have attracted immense attention of astrophysicists [11–18] owing to their importance in astrophysics and terrestrial processes [19]. Among these species, the linear cationic chains $NC_{2n}N^+$ ($n = 1–7$) have been investigated in detail both in experiment and theory [15–18]. Experimentally, Maier and co-workers observed the absorption spectra of $NC_{2n}N^+$ ($n = 1–6$) in 5 K neon matrices. Moreover, they obtained the absorption spectra and measured the higher excited electronic transitions of NC_2N^+, NC_4N^+ and NC_6N^+ in the gas phase [15]. Theoretically, Lee and Adamowicz [18] performed a preliminary study on the equilibrium geometries of ground state and vertical transition energies for the $1^2\Pi_{u/g} \leftarrow X^2\Pi_{g/u}$ transition of $NC_{2n}N^+$ ($n = 2–6$), however, their results were not accurate to some species. Consequently, we carried further studies on the system, and obtained more reliable data about their bond lengths, rotational constants, and absorption spectra [20].

However, the features of $NC_{2n+1}N^+$ clusters differ from $NC_{2n}N^+$. To our best knowledge, only Maier et al. observed the absorption spectra of NC_7N^+, NC_9N^+ and $NC_{11}N^+$ in 5 K neon matrices, and the origin bands for $1^2\Pi_{u/g} \leftarrow X^2\Pi_{g/u}$ are 629, 713 and 794 nm, respectively [17]. Lee and Adamowicz [18] predicted the structures for the ground state of NC_7N^+, NC_9N^+ and $NC_{11}N^+$ at the UHF/4-31G level and calculated the vertical transition energies for the $1^2\Pi_{u/g} \leftarrow X^2\Pi_{g/u}$ transition employing the complete active space self-consistent field method (CASSCF) and the complete active space second-order perturbation theory method (CASPT2) with DZVP basis set [21–23]. Nonetheless, some results are not consistent with experimental observations which should be carefully evaluated for the previous works.

Accordingly, in order to interpret the ground and excited states properties for these species systematically, more trustworthy theoretical calculations on the linear cationic chains are highly desirable required, especially the larger carbon chains. In our previous study, we used the CASPT2 [24] methodology to investigate the electronic spectra of $NC_{2n}N^+$ ($n = 1–7$) and obtained excellent results compared with experiment values. Therefore, we extend our investigations to the $NC_{2n+1}N^+$ ($n = 1–6$) at the same theoretical level. Here, we discuss their structural characteristic, stabilities, vertical excitation energy, and the size-dependent excited state properties. In addition, the comparison of the structures and energies with the $NC_{2n}N^+$ chains and experimental studies is also made. We expect that our calculations can provide reliable data for such system, especially for the species with the lack of experimental information.

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2. Computational details

The ground states of equilibrium geometries for $NC_{2n+1}N^+$ (n = 1–6) clusters have been optimized by the restricted coupled cluster RCCSD(T) [25–27] with 6-31G* basis set, as well as density functional calculations with the B3LYP [28–30] and CAM–B3LYP [31] functional with cc–PVTZ basis set. The level RCCSD(T)/cc-PVTZ has been used to determine the structures of $NC_{2n+1}N^+$ (n = 1–5) for a direct comparison. In addition, the CASSCF method [32,33] with 6-31G* basis set has been used to predict the geometries of the first excited state $1^2\Pi_{u/g}$ and ground state $X^2\Pi_{g/u}$ of $NC_{2n+1}N^+$ (n = 1–6). Moreover, we estimated the rotation constants by using the RCCSD(T) theory. To interpret the stabilities of the optimized linear chains, we also calculated their vibrational frequencies and the energy differences of the adjacent chains.

The CASPT2 method with the cc-pVTZ basis set has been used to determine the relative energies of the ground states and the low-lying excited electronic states at the RCCSD(T)/6-31G(d) and RCCSD(T)/cc-pVTZ equilibrium geometries for the $NC_{2n+1}N^+$ clusters. In the CASPT2 calculations, the CASSCF active spaces consist of low-energy π valence orbitals. We selected the number of the active orbitals and electrons individually for each species so as to consider the electron correlation effect, all of which are shown in Table 1. The first set of eight numbers mean the numbers of inactive (doubly occupied in each configuration) orbitals with symmetry labels A_g, B_{3u}, B_{2u}, B_{1g}, B_{1u}, B_{2g}, B_{3g}, and A_u, respectively, while the last eight numbers are the similar symmetry distribution number for the active orbitals.

Table 1
The CASSCF active spaces of $NC_{2n+1}N^+$ (n = 1–6) at the CASPT2 calculations.

Species	CASSCF active space	Electrons
NC_3N^+	(6, 0, 0, 0, 5, 0, 0, 0/0, 2, 2, 0, 0, 2, 2, 0)	9
NC_5N^+	(8, 0, 0, 0, 7, 0, 0, 0/0, 3, 3, 0, 0, 2, 2, 0)	13
NC_7N^+	(10, 0, 0, 0, 9, 0, 0, 0/0, 3, 3, 0, 0, 3, 3, 0)	17
NC_9N^+	(12, 1, 1, 0, 11, 0, 0, 0/0, 3, 3, 0, 0, 3, 3, 0)	17
$NC_{11}N^+$	(14, 1, 1, 0, 13, 1, 1, 0/0, 3, 3, 0, 0, 3, 3, 0)	17
$NC_{13}N^+$	(16, 1, 1, 0, 15, 1, 1, 0/0, 4, 4, 0, 0, 3, 3, 0)	21

The oscillator strengths (f) are calculated with the following formula:

$$f = (2/3)\Delta E|TM|^2, \quad (1)$$

where ΔE denotes the transition energy between the ground state and the excited state in atomic unit, and TM is the transition moment in atomic unit [34].

All electronic structure calculations in the present work have been carried out with the Gaussian 09 [35] and MOLPRO 2006 [36] program packages.

3. Results and discussion

3.1. Geometries and stabilities

3.1.1. The ground states geometries

The B3LYP, CAM-B3LYP, and RCCSD(T) optimized bond lengths of linear clusters $NC_{2n+1}N^+$ (n = 1–6) in their ground states are described in Fig. 1. For RCCSD(T) method, we can find that the maximum discrepancy between cc-pVTZ and the 6-31G* basis sets is 0.012 Å for $NC_{2n+1}N^+$ (n = 1–5). Thus we can see that RCCSD(T)/6-31G* is a cost-effective level of theory for the structural calculations of these species. Therefore, we predict the ground state of equilibrium geometries for $N_{13}N^+$ on this level. At RCCSD(T)/6-31G* level, we can find that the N–C bond lengths are within the 1.182–1.210 Å, exhibiting the character of triple bond, while the adjacent C–C bond lengths are in the range of 1.316–1.378 Å, bearing a dominant character of single bond. The N–C bonds are shortening and the adjacent C–C bonds are augmenting gradually by the increasing of chains.

Compared with RCCSD(T) results, both B3LYP and CAM-B3LYP predict similar bond lengths for the chains $NC_{2n+1}N^+$ (n = 1–6), and the character of bond length alternation (BLA) by CAM-B3LYP is significantly notable than those by B3LYP, which in consist with the previous studies on $C_{2n+1}Cl^+$ (n = 0–4) [37], $HC_{2n}H^+$ (n = 2–8) [38], $HC_{2n+1}H^+$ (n = 2–7) [39] and polyyne oligomers [40]. In order to get an in-depth understanding on the character of BLA, as reported in the work of bare carbon chains C_n [41], the structure of $NC_{13}N^+$ and $NC_{14}N^+$ calculated at RCCSD(T)/6-31G*

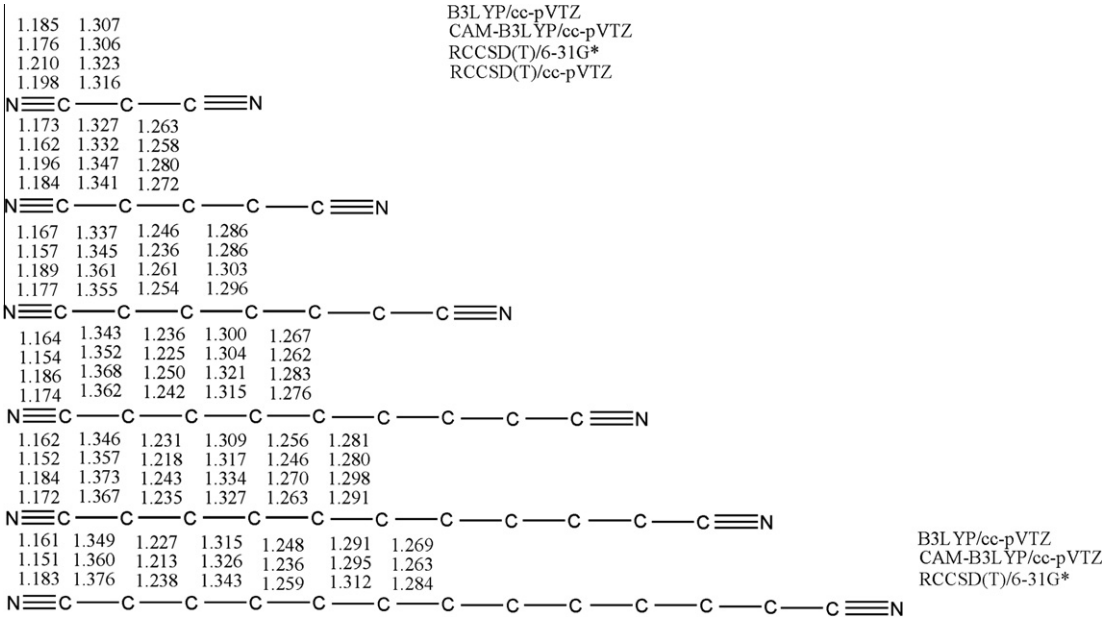

Fig. 1. The optimized bond lengths (in Å) of $NC_{2n+1}N^+$ (n = 1–6) cations by B3LYP, CAM-B3LYP and RCCSD(T) method.