Geometries and electronic structures of metastable C_2N_4 and its ions

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Abstract

We carried out the computational studies on the geometric and electronic properties of electronic states of metastable C_2N_4 (m-C_2N_4) and corresponding ions using the CASSCF and DFT(B3LYP)/CCSD(T) techniques. The optimized geometries of electronic states, vibrational frequencies, Mulliken populations, bond orders, and average polarizabilities are computed at the DFT level while the relative energies of the electronic states, ionization energy, electron affinity, binding energy of m-C_2N_4 are calculated at the CCSD(T) level. The anion photoelectron spectra of m-$C_2N_4^-$ are also predicted. It is interesting to find that the relative energies of the electronic states of m-C_2N_4 cluster linearly correlate with the amount of charge transfer between N and C atoms and that, however, there is no charge transfer between C and N atoms upon electron ionization or electron attachment.
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1. Introduction

Clusters have been intensively investigated in recent years [1–22]. It is well known that the group III–V semiconductors are applied in the fabrication of fast microelectronic devices. Thus, the geometries, electronic structures, and spectroscopic properties of mixed III–V group clusters have been the focus of many theoretical and experimental studies [9–12,19,20].

Since Liu and Cohen [23] have predicted that some of the crystalline forms of C_3N_4 might have values of bulk modulus close to, or even greater than, that of diamond, the synthesis, structure, and property of carbon nitride have been the topic of many theoretical and experimental studies [23–29]. C_3N_4 has several different phases [27], that is, β-C_3N_4, α-C_3N_4, C_3N_4 defective zinc-blende structure with carbon vacancies, cubic C_3N_4, and two graphite-like rhombohedral forms. Various other carbon nitride compounds and structures can exist [27]. On the other hand, carbon nitrides are widely used in hardness and photoelectric materials. Therefore, systematic studies of the geometries and electronic structures of carbon nitride clusters are very significant for gaining insight into the growth mechanism of carbon nitride nanomaterials.

So far, there are no theoretical and experimental data available on geometries and low-lying electronic states of metastable C_2N_4 (m-C_2N_4) cluster. In this work, the low-lying electronic states of m-C_2N_4 and its ions have been investigated using the CASSCF and DFT(B3LYP)/CCSD(T) methods. The Mulliken populations, leading configurations, compositions of molecular orbitals, and bond orders are employed to explore the nature of bonding in these clusters. The ionization energies, electron affinities, and binding energies of m-C_2N_4 cluster, the anion photoelectron spectra of the corresponding anion cluster are also predicted, which can provide some useful information for experimental study of this cluster. On the other hand, it is interesting to note that the relative energies of the low-lying electronic states of m-C_2N_4 linearly depend on the amount of charge transfer between C and N atoms.

2. Methods of calculation

In order to search the low-energy isomers of C_2N_4, the initial structures of C_2N_4 are set at various possible structures. Then, these structures are fully optimized at the DFT(B3LYP) level. Finally, the CCSD(T)/6-311 + G(d) method is used to calibrate

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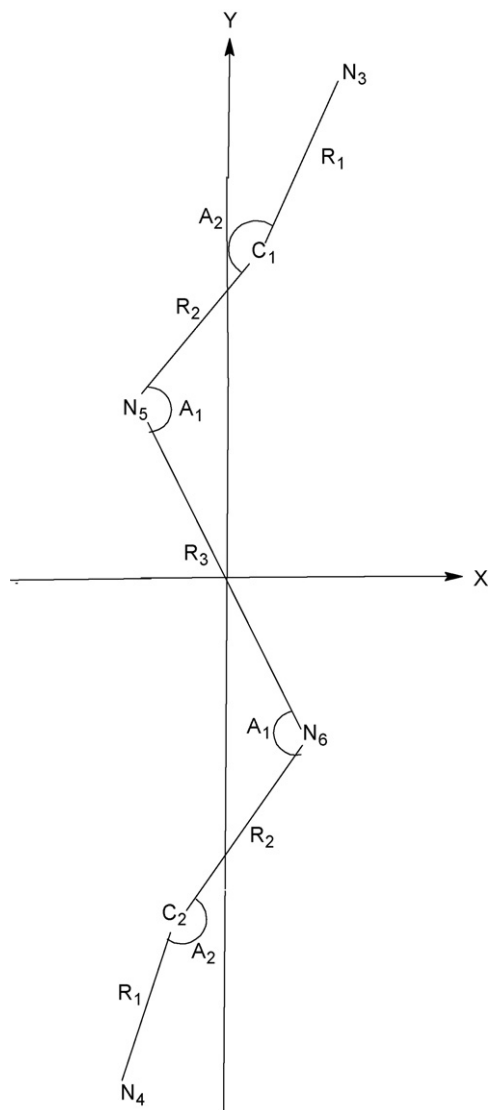*E-mail address:* xlzhu@njut.edu.cn (X. Zhu).

Fig. 1. Equilibrium geometry for the low-lying electronic states of metastable C_2N_4 (m-C_2N_4) with C_{2h} symmetry.

the energies of these structures. So far, 15 low-energy isomers have been found. The structure of a metastable C_2N_4 (m-C_2N_4) is shown in Fig. 1. Other low-energy isomers of C_2N_4 obtained at the DFT level are to report elsewhere.

First-principle calculations [26] predict that β-C_3N_4 crystal is a metastable structure. In fact, carbon nitrides have several metastable structures [27] as mentioned above. It can be predicted that the metastable m-C_2N_4 cluster will be obtained and studied experimentally.

In this work, we focus on the m-C_2N_4 with C_{2h} point group. The initial structures of the low-lying electronic states of m-C_2N_4, cation, and anion are set at C_{2h} symmetry. First, optimizations are carried out on these structures with the constraint of C_{2h} point group at the CASSCF level. Second, the CASSCF geometries are further optimized at the DFT(B3LYP) level. Then, vibrational frequency calculation is performed at the same level to examine whether the optimized structures of these states are stable or not. Finally, in order to obtain accurate energy ordering,

the energies of these states are calibrated at the CCSD(T)/RECP and CCSD(T)/6-311 + G(d) levels, respectively.

The relativistic effective core potentials [30–32] (RECPs) are applied that retains the outer $2s^2 2p^2$ and $2s^2 2p^3$ shells of C and N atoms in the valence space, respectively. The rest electrons are replaced by the RECPs. Gaussian basis sets are taken from Ref. [33]. The RECPs basis sets of both C and N are (4s4p). In the CASSCF calculations, 28 valence electrons of the neutral m-C_2N_4 (27 for cation, 29 for anion) are distributed in all possible ways among 17 active orbitals, which includes $7a_g$, $6b_u$, $2a_u$, and $2b_g$ orbitals.

The CASSCF and DFT/CCSD(T) computations are performed using GAMMESS [34] and GAUSSIAN [35] packages, respectively.

3. Results and discussion

Fig. 1 displays the optimized structure of the low-lying electronic states of m-C_2N_4, which exhibits a planar geometry with C_{2h} symmetry at the CASSCF and DFT levels. Table 1 displays the optimized geometry parameters of the low-lying electronic states of m-C_2N_4. It is not difficult to see from Table 1 that there is no large Jahn–Teller distortion upon electron excitation. As shown in Table 1, the values of A_1(N$_5$–N$_6$–C$_2$, or N$_6$–N$_5$–C$_1$) are between 99.9 and 138.6°, demonstrating that the N$_5$ (or N$_6$) atoms exhibit sp^2 hybridization, while the values of A_2(N$_4$–C$_2$–N$_6$ or N$_3$–C$_1$–N$_5$) are between 169.4 and 180°, suggesting that C$_2$ (or C$_1$) atoms exhibit sp hybridization. The N$_5$–N$_6$ bond distances for the electronic states listed in Table 1 are 1.216–2.583 Å, which are longer than the N–N bond length (1.118 Å) of N$_2$ molecule as expected. The N$_6$–C$_2$ bond distances are 1.252–1.363 Å, while the N$_4$–C$_2$ bond distances are 1.175–1.264 Å. The C–N bond length in isolated CN cluster is 1.259 Å at the DFT(B3LYP)/RECP level. It reveals that C$_2$–N$_6$ bonding interaction is weakened when the N$_6$ and C$_2$ atoms are combined with N atoms, while N$_4$–C$_2$ bonding interaction is enhanced when the C$_2$ atom is combined with the N$_6$ atom. The bond orders between atoms in m-C_2N_4, m-$C_2N_4{}^+$, and m-$C_2N_4{}^-$ are listed in Table 2. It is interesting to find from Table 2
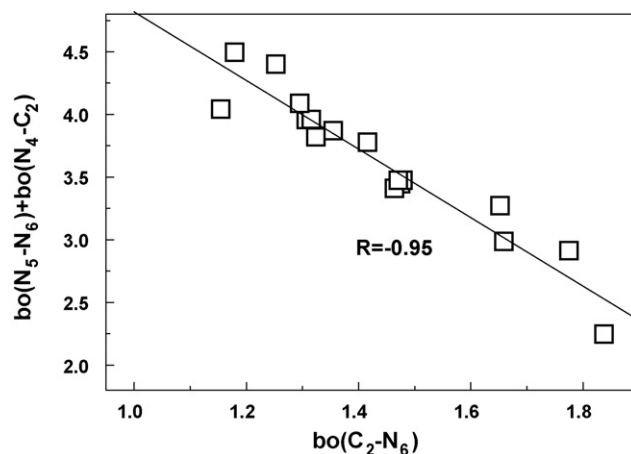

Fig. 2. Correlation of summation of bo(N$_5$–N$_6$) and bo(N$_4$–C$_2$) with bo(C$_2$–N$_6$).