Structure and stability of $(\text{AlN})_n$ clusters

WU Haishun (武海顺)$^1$, ZHANG Congjie (张聪杰)$^{1,2}$, XU Xiaohong (许小红)$^1$, ZHENG Lansun (郑兰荪)$^2$ & ZHANG Qian’er (张乾二)$^2$

1. Department of Chemistry, Shanxi Normal University, Linfen 041004, China;
2. Department of Chemistry, Xiamen University, Xiamen 361005, China

Correspondence should be addressed to Wu Haishun (email: wuhs@dns.sxtu.edu.cn)

Received August 1, 2000

Abstract  AlN and Al$_2$N$_2$ have been observed in the record of time-of-flight mass-spectra as positive ions. Associating with density functional theory (DFT) B3LYP method with 6-31G* basis set, we have carried out the optimizing calculations of the geometry, electronic state and vibrational frequency for $(\text{AlN})_n$ ($n = 1\sim15$) clusters, moreover, discussed the character of the chemical bond and thermodynamical stability and explained the experimental mass spectra. The results show that there do not exist Al-Al and N-N bonds and only exists Al-N bond in the ground state structures of $(\text{AlN})_n$ clusters; and the "magical number" regularity of $(\text{AlN})_n$ is those whose atom number is 4, 8, 12, 16, 20, etc, all of which are times of four.

Keywords: $(\text{AlN})_n$ clusters, TOF mass-spectra, density functional theory, structure and stability, vibrational frequency.

AlN ceramic material has many excellent physical and chemical properties, such as high thermoconductivity, low thermal-inflate coefficient and large energy gap, which have aroused universal attention$^{[1\sim4]}$ of physicists, researchers of materials and chemists. Under the vacuum condition, the sputtering Al reacts with nitrogen to prepare the new-type AlN nanofilm by using magnetron reactive sputtering (MRS) technique. It is easy for MRS technique to form precursor intermediate complexes, and a series of Al$_n$N$_m$$^{[4]}$ clusters had already been observed. Lynam$^{[5]}$ studied the structure of H$_2$AlNH$_2$ with GVB/DZP method; Davy$^{[6]}$ obtained the stable geometries of HAINH and H$_2$AlNH$_2$ at CCSD/TZ2P level; Müller$^{[7]}$ calculated the electronic structure and IR spectrum of Me$_2$AlNH$_2$ using the second-order Moller Plesset (MP2) theory; and Matsunage et al.$^{[8]}$ used ab initio theory to study the structure similar to benzene molecule, prism, boat and chair form of (XAlNH)$_3$ and found that such a structure as benzene molecule form is the most stable structure. Alexey et al.$^{[9]}$ studied the structure and thermodynamical stability of X$_m$(AlN)$_n$H$_m$ serial clusters at SCF/DZP level and discussed the formation mechanism of $(\text{AlN})_n$ clusters. Recently, Nayak et al.$^{[10]}$ chose GGA and LSDA methods to discuss the properties of chemical bond of $(\text{AlN})_n$ clusters. And Grimes$^{[11]}$ adopted local density functional (LDF) method to study the structure and physical and chemical properties of $(\text{AlN})_n$ ($n = 1\sim4$), and obtained the relationship between the variation of the properties of the cluster and the increase of $n$.

To further clarify the mechanism of AlN nanofilm formation from clusters, to explore the stable regularity of $(\text{AlN})_n$ clusters, and to direct the experiments of preparation with the pulsed
laser and MRS technique, in this article, we associate TOF mass-spectra with DFT to carry out some studies on theory and experiment for (AlN)\textsubscript{n} in which \( n = 5 \rightarrow 15 \) has not been reported theoretically up to now, and for the first time their “magical number” regularity is presented.

1 Experimental and theoretical methods

1.1 Experimental method

Many kinds of clusters can be produced by laser ablating the AlN powder sample\textsuperscript{[12]}. The accomplishment of the experiment employed the apparatus of the State Key Laboratory for Physical Chemistry of Solid Surface in Xiamen University. The apparatus has been described in detail elsewhere. And hence only a brief description is presented here. The aluminium-nitrogen cluster ions were produced by laser ablating the AlN powder sample. The pulsed laser beam selected for the experiment is the second harmonic output of a Quantary Nd:YAG laser (532 nm wavelength, 7 ns pulse width), and was gently focused with a lens (\( f = 80 \text{ cm} \)) to approximately a 1 mm spot on the sample with the power density on the order of \( 10^8 \text{ W/cm}^2 \). The sample, AlN powder, was pressed into the sample holder before experiment. The supersonic molecular beam was controlled by a pulsed valve. When the valve was inactive, the whole vacuum system was operated under a vacuum of \( 2 \times 10^{-9} \text{ Pa} \).

1.2 Computational method

First of all, these geometries of (AlN)\textsubscript{n} (\( n = 1 \rightarrow 15 \)) were optimized using \textit{ab initio} HF/STO-3G method to obtain the roughly initial guess and further optimized using the same method with 6-31G* basis set. Based on the last optimizing results, we finally adopted DFT B3LYP method with 6-31G* to optimize these geometries and calculate the vibrational frequency. All the calculations were made with Gaussian 98 software and were completed in SGI/O2 workstation.

2 Results and discussion

2.1 TOF mass-spectrum of positive and negative ions of (AlN)\textsubscript{n}

Time-of-flight mass spectrum of positive ions produced by laser ablating the AlN powder sample is shown in fig. 1, in which only three mass spectra peaks of Al\textsubscript{1\textsuperscript{n}}N\textsubscript{m} clusters, Al\textsubscript{1}N\textsuperscript{+}, Al\textsubscript{2}N\textsuperscript{+} and Al\textsubscript{2}N\textsubscript{2}\textsuperscript{+} are observed. Especially, we first found the mass spectra peaks of Al\textsubscript{2}N\textsubscript{2}\textsuperscript{+} which are