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Systematic study of small BN clusters

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Abstract. We performed a systematic investigation of the small B_xN_y ($x+y \leq 6$) clusters using the *ab initio* Hartree-Fock scheme plus second-order perturbation theory. The nature of the potential energy surface extrema are analyzed through analytical total energy second derivatives. Ionization potentials, binding energies and the stability against some possible reaction mechanisms are calculated. Based on these results we propose that the growing process for these clusters is mainly due to the successive incorporation of BN molecules. A discussion of some mass spectrometry experimental results is also presented.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Qv Stability and fragmentation of clusters

1 Introduction

The last two decades have seen a great development in the area of small particles and nanosystems. Theoretical and experimental studies revealed the properties of a diversity of these new systems whose interest lies mainly on the fact that their properties are size dependent. This characteristic feature makes clusters a suitable field to the search of materials exhibiting new and specific properties.

Among the possible clusters, the elemental ones are obviously the simplest and have been the most extensively studied and characterized. In fact, much is known today about elemental clusters of alkali metals, noble gases, carbon, silicon and gold among others [1,2]. Binary clusters present an additional difficulty, as compared to the elemental ones. This is related to the fact that, for a given configuration of a N-atom clusters, there will be $N+1$ compositional possibilities for binary clusters and only one for elemental clusters. Obviously, the complexity increases as one goes on clusters composed of three, four etc., different elements.

Our interest here is centred on small binary boron nitride clusters. Two main reasons guided us in this study. The first and more basic one is to understand the properties of these systems with the variation of their sizes. It is expected to be possible to extract some physical rules that could explain the process by which the properties change until their bulk values. Secondly, we aim to be able to characterize the molecules present in the growing process of thin films of cubic boron nitride. This material exhibits very interesting properties for both coating and electronic devices like extreme hardness, low chemical reactivity, high thermal conductivity etc. [3].

These clusters have, in fact, already been experimentally [4-8] and theoretically studied [9,10]. In these theoretical studies, however, the authors focused mainly on the characterization of each individual clusters. Here we are interested at the general behavior of these clusters as one changes their composition and/or number of atoms. In section 2 we present the adopted theoretical methodology. Section 3 briefly presents the results for each cluster together with an analysis of some fragmentation reactions and a discussion of the experimental results. Finally, our conclusions are presented in section 4.

2 Methods

We employed the same theoretical methodology to study all the considered clusters. This allow us comparisons among the results for the different species. The molecular orbitals are represented by a linear combination of a double-zeta quality basis set [11] incremented by two polarization functions. For the open shell systems we start the calculations within the UHF scheme. However, in the presence of a significant spin contamination, the ROHF scheme was adopted. The geometry optimization procedure started from several different highly symmetric polyhedra obtained using the Polya's theorem [12]. No symmetry constraints are imposed on the wavefunction during the geometrical search. The nature of the obtained potential energy surface extrema are analyzed through analytical total energy second derivatives and the harmonic vibrational frequencies are determined [13]. Once found the local minima, a second order perturbation theory (MP2) calculation is performed to evaluate the electronic correlation contributions and to obtain ground state configurations.

All calculations are performed using the GAMESS code [14].

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Table 1. Calculated total electronic states, interatomic distances, point group symmetries and fragmetation enthalpies, in eV, for the studied clusters. Positive (negative) values indicate that the cluster will dissociate (not dissociate) under the specific reaction.

Species	Term	Distances (Å)					Point group	Fragmentation enthalpies (eV)				
B_xN_y		(1-2)	(2-3)	(3-4)	(4-5)	(5-6)		$(X+N_2)$	(X+N)	(X+B)	(X+BN)	$(X+B_2)$
B_2	$^3\Sigma_g^-$	1.68					$D_{\infty h}$			−2.01		
BN	$^3\Pi$	1.32					$C_{\infty v}$		−3.14	−3.14		
N_2	$^1\Sigma_g^+$	1.10					$D_{\infty h}$		−7.29			
B_3	$^2A_1'$	1.61					D_{3h}			−3.94		−3.94
B_2N	$^2\Sigma_u^-$	1.32					$D_{\infty h}$		−1.55	−9.13	−9.13	
BN_2	$^2\Pi_g$	1.31					$D_{\infty h}$	0.08	−4.81	0.08	−6.90	
B_4	$^1A_{1g}$	1.55					D_{4h}			−5.43		−7.60
B_3N	$^1\Sigma^+$	1.80	1.26	1.39			$C_{\infty v}$		−5.74	−8.42	−10.25	−10.25
B_2N_2	$^3\Pi$	1.32	1.36	1.26			$C_{\infty v}$		−3.26	−5.48	−12.96	
BN_3	$^1\Sigma^+$	1.10	1.43	1.24			$C_{\infty v}$	−5.59	−5.10		−5.59	
B_5	$^2A_2$	1.60	1.57	1.59			C_{2v}			−3.33		−7.00
B_4N	$^2A''$	1.34	1.38	1.68	1.55		C_s		−3.07	−2.77	−9.09	−3.90
B_3N_2	$^2\Sigma^+$	1.30	1.31	1.32	1.30		$C_{\infty v}$		−5.98	−5.60	−9.44	
B_2N_3	$^2\Pi$	1.38	1.26	1.36	1.20		$C_{\infty v}$	2.20	−0.97	−1.35	−7.03	
BN_4	$^2\Pi$	1.17	1.32	1.33	1.17		$C_{\infty v}$	1.12	−1.94			
B_6	^3A_u	1.65	1.69	1.56			C_i			−3.86		−5.43
B_5N	$^1A_1$	1.52	1.64	1.36			C_{2v}		−6.06	−6.31	−9.97	−7.33
B_4N_2	$^1\Sigma_u^+$	1.40	1.26	1.64			$D_{\infty h}$		−7.85	−4.65	−11.20	
B_3N_3	$^1A_1'$	1.36					D_{3h}		−4.91	−9.50	−11.09	
B_2N_4	$^1A_1$	1.09	1.53	1.38	1.49	1.33	C_1	1.10	−4.34	−3.75		
BN_5	$^1A_1$	1.09	1.59	1.55	1.23	1.63	C_1	4.05	−0.41			

3 Results

Table 1 presents the point group symmetries, total electronic states, the calculated reaction enthalpies for some fragmentation processes involving the studied clusters, and the interatomic distances related to the schematic representation of the minimum energy configurations shown in figure 1.

Noteworthy is the fact that, although we employ a not so elaborated correlation approach (MP2) in our calculations, the results presented in table 1 are seen to be in good agreement with those obtained using more sophisticated and computationally demanding correlation methods [9]. The special case of diatomic molecules shows to be the most difficult to pursue through the adopted approach. Except for the N_2 molecule, which presents no problems in finding the correct ground state, the other two required a careful investigation. For each starting geometry, *i.e.*, at each considered initial interatomic distance, and they were several, we performed optimization calculations on a set of different electronic configuration. Applying this methodology we found a $^1\Sigma^+$ state as the ground state for the BN molecule, with a $^3\Pi$ state 0.24 eV (5.53 kcal/mol) above in energy. However, it is accepted today that the $^3\Pi$ is actually the ground state, being very close in energy to the $^1\Sigma^+$ [15]. We will then use this $^3\Pi$ state in our subsequent analyzes, as shown in table 1. The optimization procedure for the B_2 molecule showed to be very sensitive to the starting interatomic distance. Despite this fact, we found the correct $^3\Sigma_g^-$ ground state. The B-B distance was found 5% longer than experimental value [16].

The triatomic molecules also required a careful examination of the potential energy surface. In this case, however, the results present a more favorable comparison with previous calculations [9]. For the other studied clusters we found no great problems in obtaining our final structures, even in cases where a symmetry breaking due to a Jahn-Teller distortion is expected to occur [9]. As can be seen from table 1, the resulting structural changes induced by the Jahn-Teller effect are really very small. This general good behaviour of the obtained results give us confidence to proceed with our analyzes.

In the case of the $B_xN_y \rightarrow B_xN_{y-2} + N_2$ fragmentation process, we present the results only to those clusters where a N_2 molecule clearly appears as a distinct subsystem. This allow us to build a simple and reasonable reaction path for each considered case. From table 1 one can see that, except for the case of BN_3, all the N-rich clusters dissociate under this reaction. This would indicate the ausency of N-rich clusters in the observed mass spectra, at least in the gas phase.

We now analyse the results for the other considered fragmetation reactions shown in table 1, those in which one of the products is a B or N atom or a B_2 molecule. For the cases involving the B_2 as a product we apply here the same restrictions as earlier, *i.e.*, we consider only those parent cluster where the B_2 molecule appears as a distinct subsystem. Let us think, however, of the reverse reactions, *i.e.*, those describing an association process. It turns clear

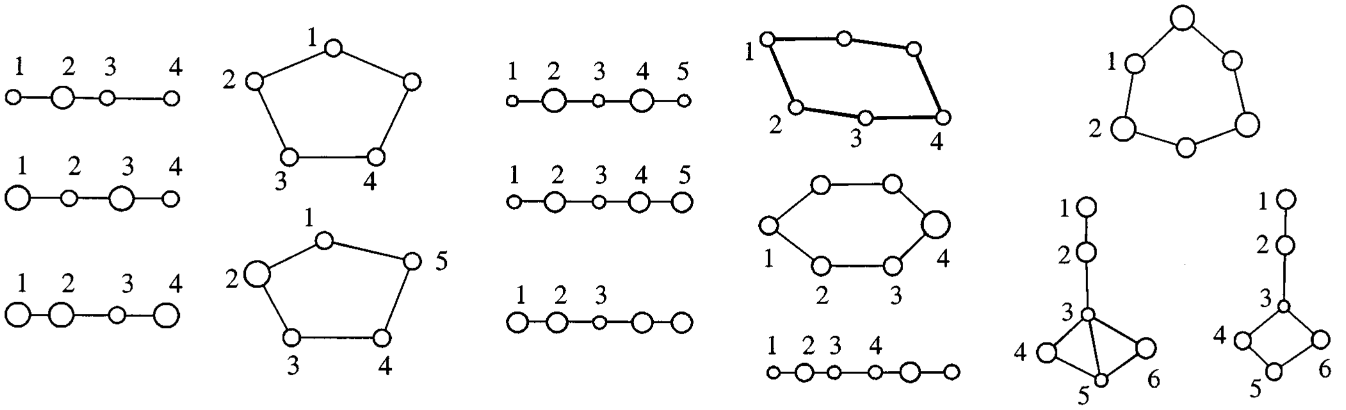

Fig. 1. Schematic representations of the geometrical structures for the studied BN clusters not obviously deduced from its point symmetry group. The bigger (smaller) circles represent the N (B) atoms. The distances between the numbered atoms are given in table 1.

from the values in table 1 that, for a given initial seed, the system will prefer to increase incorporating diatomic molecules. The association processes involving the absorption of a single atom are seen to be less probable.

Among the growing processes involving the incorporation of a diatomic molecule, those occuring with the addition of a BN molecule are energetically favorable, as shown in table 1. If we take, *e.g.*, the BN molecule as the choose initial seed, the system's energy gain will be greater for the following growing path: BN $\rightarrow$ B_2N_2 $\rightarrow$ B_3N_3. The same thing will occur when we take B_2, B_2N or B_3N as seed clusters. The exception again is the BN_3 molecule. It is interesting to note that this molecule arises from the incorporation of a BN molecule by the highly stable N_2 molecule. The possible clusters generated from BN_3 by one the considered reactions will, once satisfied the restrictions posed above, dissociate loosing a N_2 molecule.

Secondly in energy is the association process where a B_2 molecule is incorporated. For the atom-by-atom growing processes, the calculated reaction enthalpies in table 1 indicate no special rules.

Becker and Dietze [4] performed a mass spectrometry analyses on positively charged BN clusters. They analysed the relative stabilities of some sequences of clusters. We will restrict us only to the results concerning the B_xN_y $(x + y \leq 6)$ clusters.

For B_xN^+, $B_xN_2^+$ and $B_xN_3^+$ clusters they found the following stability order:

a) $B_3N^+ > BN_3^+ > B_2N_2^+$,
b) $B_3N_2^+ > B_4N^+ > B_2N_3^+$,
c) $B_4N_2^+ > B_5N^+ > B_3N_3^+$.

For BN_y^+, $B_4N_y^+$ and $B_5N_y^+$ clusters they found:

a) $BN_3^+ \approx B_4^+$,
b) $B_4N^+ > B_5^+ > BN_4^+$,
c) $B_4N_2^+ > B_5N^+ > BN_5^+$.

Finally for $B_2N_y^+$ and $B_3N_y^+$, they found:

a) $B_2N^+ > B_3^+$,
b) $B_3N^+ > B_2N_2^+$,
c) $B_3N_2^+ > B_2N_3^+$,
d) $B_2N_4^+ \approx B_3N_3^+$.

We note here that we can not directly use the calculations for neutral clusters to perform a direct comparison with the experimental results for the positively charged clusters. The ionization process will certainly involve a posterior electronic and even ionic relaxation. Taking it into account, we have calculated the binding energies for the positively charged clusters in the following manner. Starting from the minimum energy configuration for a given neutral cluster, we extracted an electron and performed a geometry optimization followed by a MP2 correlation correction on the found equilibrium structure. The binding energies were then obtained by the following expression:

$$E_b(B_xN_y^+) = E(B_xN_y^+) - (x-1)*E(B) - y*E(N) - E(B^+),$$

where $E_b(X)$ and $E(X)$ are the binding and total energies of X, respectively. Here we suppose that the electron is being extracted from a B atom. This supposition makes no difference at all. Looking at the obtained results in table 2, one can easily see that, except for the cases of $B_4N^+ > B_5^+$ and $B_4N^+ > B_2N_3^+$, all other stability order relations are well reproduced. Given the used approximations, this result is impressive.

Becker and Dietze [4] also showed that the stability of clusters obtained from B_2N by sequentially adding BN molecules will be greater than that obtained by the same procedure taking however B_2 as the starting cluster. Dividing the binding energies of $B_3N_2^+$ and B_3N^+, given in table 2, by the number of atoms in each of these cluster, it results that the experimentally observed stability order is clearly satisfied. The same occurs between $B_3N_2^+$ and $B_4N_2^+$, B_2N^+ and B_2^+ and finally between B_2N^+ and B_3N^+. This result give an additional support to the hypothesis of a growing process obtained by the successive incorporation of BN molecules.

Table 2. Calculated vertical ionization potentials for neutral clusters, IP_v, and binding energies, E_b, for the positively charged clusters, in eV.

Species	IP_v (eV)	E_b (eV)
B_3	8.42	−5.20
B_2N	8.07	−8.40
BN_2	10.38	−3.86
B_4	10.81	−8.62
B_3N	8.19	−9.41
B_2N_2	9.59	−3.04
BN_3	11.76	−8.50
B_5	11.88	−15.60
B_4N	8.31	−14.03
B_3N_2	3.27	−22.02
B_2N_3	5.60	−15.21
BN_4	9.13	−9.12
B_6	7.65	−18.48
B_5N	9.07	−19.61
B_4N_2	9.70	−20.92
B_3N_3	11.29	−19.46
B_2N_4	8.65	−15.75
BN_5	6.42	

The vertical ionization potentials for the studied clusters are shown in table 2. These values were obtained from a total energy difference between the neutral and the positively charged cluster, where the structure of the both clusters are that of the former.

La Placa *et al.* [8] used a 193 nm (6.42 eV) UV laser to generate positively charged BN clusters from a previously formed BN plasma. They reported the observation of only BN and B_2N clusters. The observation of the calculated vertical ionization potentials presented in table 2, turns clear why almost no BN-mixed cluster were observed. The used ionization laser energy is not enough to ionize the greater majority of the BN cluster, with the exception of $B_3N_2^+$ and $B_2N_3^+$ clusters. The last of these two clusters should, according to our calculations, dissociate into B_2N + N_2 molecules.

4 Conclusions

Using a systematic approach we studied the whole set of B_xN_y $(x + y \leq 6)$ clusters. The results are seen to be in good agreement with previous more demanding calculations, even in the more difficult cases.

With exception of BN_3, all N-rich clusters dissociate lossing a N_2 molecule. The BN_2 molecule is seen to be almost isoenergetic with B + N_2.

Some fragmetation reaction enthalpies are calculated and a growing route for these small clusters by successive incorporation of BN molecules is stablished. The growing process can also be obtained by adding B_2 molecules, although it is seen to be less probable.

The calculated binding energies for the positively charged clusters are shown to reproduce various sequences of stability order among these clusters, as observed in mass spectrometry results.

An explanation is also given to the ausency of BN-mixed cluster in an experiment using a low energy UV laser to ionize a BN plasma generated by laser ablation.

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