Dissociation mechanisms of cluster ions resolved using *ab-initio* molecular orbital calculations

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Abstract

We have examined the cluster-size effect on fragments in the collision-induced dissociation (CID) of small boron clusters (B_n^+, $n \leqq 8$) by means of *ab-initio* molecular orbital (MO) calculation, for conditions representative of low-Z cationic clusters in plasma. Single cations B^+ (leaving B_{n-1}^0) are predominantly fragmented from small clusters B_n^+ ($n < 5$) by low-energy collisions (<10 eV) with Xe atoms. With increasing the size n, beyond $n = 5$, B_{n-1}^+ (leaving B^0) clusters are observed preferentially. This alternating trend in experiment has not been quantitatively explained by previous *ab-initio* MO calculations. We used a density functional method called B3LYP and basis functions 6-31+G** including diffuse functions, and have succeeded in reproducing the alternation of the competing two dissociation processes as cluster size increases. In addition, the accuracy of ionization potentials and binding energies were also improved.
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1. Introduction

Inside a plasma reactor, molecules (neutral or charged clusters) continuously collide with wall material and each other. These clusters are mainly composed of low-Z atoms. Kinetic or electrostatic energy transfer in collision events takes various reaction paths and their outcome in terms of com-position, decomposition (dissociation), excitation, ionization, or mixtures of these, depending on the relative velocity between the two molecules, the transferred energy, and their chemical activity that is determined by electronic states concerned.

The present investigation concerns low-energy collisions of small clusters composed of low-Z atoms with inert atoms. Here B_n^+ clusters collide with Xe atoms at energies below 10 eV, where only dissociation is experimentally observed. The cross-section monotonously increases with increasing collision energy, suggesting the kinetic energy transferred in *elastic collisions* detaches a single B^0 or

B^+ particle from the initial B_n^+ cluster. In other words, no chemical reactions with target atom do take place.

Two dissociation fragments were observed, for small B_n^+ clusters below $n = 8$ [1], although a third fragment could be observed for much larger clusters, e.g. $n = 13$. As cluster size increases, first single-particle B^+ was preferentially detached, then above $n = 5$, B^0 detachment became dominant.

Note that in the case of chemically active targets, like O_2 [2] or D_2 [3] molecules, B_mO^+ or $B_mD_{m'}^+$ ($m \leqslant n$ and $m' = 1$ or 2) were observed with the $B_{n-m'}^+$ ($m' = 0$–3), i.e., chemical reactions occurred for boron clusters with target atoms. The cross-section of each reaction path changed acutely depending on collision energy, and the dependency was individual for each channel of chemical reaction. Such behavior implies that the reaction passed through the *quasi-molecular state* comprising e.g. B_n^+, O_2, and D_2. For such situations, another scheme of coupled-channel method must be used, which solves the time (or velocity)-dependent reactions and fragments produced.

Here we examine the kinetic property of *collision-induced dissociation* (CID) process of clusters caused by inert target atoms using *ab-initio* molecular orbital (MO) calculations, for the case of cationic boron clusters colliding with Xe atoms. Strictly speaking, colliding molecules temporarily form a so-called quasi-molecule and new energy scheme can open a new path crossing initial and final states as Fano–Lichten processes. The details of such chemical reaction process if both association and dissociation occur during collisions should be solved using time-dependent MO calculations, particularly taking into account the relative velocity and distance at each time-step. On the contrary, if solely dissociation occurs, we can predict the collision paths both from initial and final states that can be determined by MO calculations assuming stable states, without invoking time-dependent MO calculations. Many *ab-initio* MO calculations have been performed to explain such CID phenomena.

The *ab-initio* MO calculation has been improved with regard to both the adopted algorithm and basis functions. For the study of CID of B_n^+ colliding with inert Xe atoms, several calculations have been reported. For example, previously restricted configuration interaction (CI) [1], perturbation theory up to 4th order MP4 [4,5] was used, where best level of basis functions was the set of 6-31G. We have used B3LYP (Becke type 3 parameters density func-

tional method with the Lee-Yang–Parr correlation function) in Gaussian-03 [6] with 6-31+G** one of the best basis functions. In fact, the combination of the algorithm and basis functions governs the values determined from the total energy E_T. Previous calculations of dissociation energies did not explain the dependence on cluster-size effect on the fragmentation, although some dissociation energies were close to measured data.

2. Methods

2.1. The stable geometry of boron clusters

The stable structure of a cluster should fulfill the necessary and adequate condition that the corresponding point of the potential energy surface (PES) should be a local minimum. That is, the PES has a minimum value and concave behavior. This is commensurate with the lowest value of total energy (E_T) and the absence of imaginary frequencies in molecular vibrations about the point. Imaginary frequencies included in the molecular vibration modes, reveal the presence of saddle points on the PES. Realistic molecular vibrations of a stable cluster correspond to real frequencies within the so-called fingerprint region (usually 600–1300 cm^{-1}). Thus unstable structures can be excluded from candidate structures. These rules are commonly used to assign the local minimum on PES [5,7,8], except for early study of Hanley et al. [1] and Ray et al. [4] who judged the stability of a cluster only by seeking the lowest value of E_T. The 'local minimum' cannot be always unique, for example, the B_{12} cluster can have ichosahedron structure with high symmetry, while one can reasonably reach another local minimum of the PES [5,7] with lower value of E_T.

We have used the fully optimized density functional method of the B3LYP algorithm and basis functions 6-31+G** including diffuse functions. Often algorithms of MP2, MP4, UCIS and UCISD (Unrestricted Configuration Interaction with single (and double) excitation) were also investigated for comparison with previous literature reports. The use of both better algorithm and basis functions have increased the reliability of calculations as will be seen in the results shown in Section 3.

2.2. Derived quantities from the total energy E_T

From the values of E_T for each type of cluster, some physical quantities were calculated.

The ionization potential energy of a B_n cluster, IP(n), and binding energy of B_n, $E_B(n)$, are given by

$$IP(n) = E_T(B_n) - E_T(B_n^+), \qquad (1)$$

$$E_B(n) = \frac{1}{n}\{n \cdot E_T(B) - E_T(B_n)\} \quad \text{for } B_n^0,$$

$$E_B(n) = \frac{1}{n}\{(n-1) \cdot E_T(B) + E_T(B^+) - E_T(B_n^+)\}, \quad (2)$$

for B_n^+.

For the experiment [1] we assume CID produces two kind of fragments, i.e., $B_n^+ \rightarrow B_m^+ + B_{n-m}^0$. Then the dissociation energy, $\Delta\varepsilon_{nm}$, is given by for all the probable value m,

$$\Delta\varepsilon_{nm} = E_T(B_m^+) + E_T(B_{n-m}^0) - E_T(B_n^+), \quad n > m \geqslant 1. \qquad (3)$$

3. Results

3.1. To define the stable structures

We defined the geometrical structures of cationic or neutral clusters, when local minimum in PES was confirmed. All structures of cationic or neutral boron clusters were planar or nearly planar. This result differed from previous calculations, one used RCISD (Restricted Configuration Interaction with single and double excitation) with 6-31G [1] while another used UHF-MP4 with 3-21G* [4]. Our calculations are, however, consistent with previous report of Boustani [8] and Kato using the UHF-MP4 with 6-31G** basis set. The structures for cationic clusters were linear B_2^+, regular triangle B_3^+, rhombus B_4^+, regular pentagon B_5^+, laterally expanded hexagon B_6^+, nearly capped hexagon B_7^+, and slightly deformed and capped heptagon B_8^+. Neutral clusters

almost had similar structure to the corresponding cationic one. Exceptions were in the change of symmetry, B_5^0 from D_{5h} to C_2 to a flabellate-like plane, B_6^0 from D_{2h} to C_{2h} flabellate-like plane, and B_8^0 from D_{2h} to a wheel-like D_{7h} as reported by others [9]. All the molecular frequencies were within the fingerprint region.

The reasons for the discrepancy of recent calculations from pervious ones are (1) frequency analysis is naturally included, (2) a more sophisticated algorithm is used, and (3) more sophisticated basis functions are used. For example, the previous calculations proposed different atomic configurations from our results, e.g., linear B_4^0, bipyramid B_5^0 and B_5^+, or a rather three-dimensional frame, these exhibited imaginary frequencies or higher values of E_T than our present results. For the structure B_4^0, we found a rhombic structure, which is consistent with a recent report [10].

3.2. Reliability of calculation

Table 1 compares the calculated value of the ionization potential (IP) for B_n^0 clusters with measured data. The IP value is different for each size of clusters, thus in order to estimate the accuracy for a sequence of calculations with different methods, we took the average of the relative errors obtained for each size of cluster. Namely, for a group including N cases with different size of boron clusters, we estimate the relative error (%) as an averaged value

$$\sigma(IP) \equiv \langle \text{relative errors} \rangle$$

$$= \frac{1}{N} \sum_{i=1}^{N} \frac{|IP_i(\text{Cal.}) - IP_i(\text{Expt.})|}{IP_i(\text{Expt.})} \times 100. \qquad (4)$$

Table 1
Comparison of calculated with experimental [1] ionization potentials (IP) (eV) of neutral boron clusters (B_n^0)

References	[1]	[1]	[4]	[5]	Present work					
		RCIDS	MP4	MP4	UHF	MP2	MP4	CIS	CISD	B3LYP
Cluster size	Expt.	6-31G	3-21G*	6-31G*			6-31+G**			
1	8.298	7.946		7.840	7.948	8.026	7.947	8.026	7.887	8.683
2	10.400	8.376	6.813	8.814	5.640	7.851	7.757	7.890	7.366	8.018
3	9.700	8.523	8.960	8.482	9.453	8.693	9.146	8.691	9.354	9.806
4	9.800	8.095	14.390	9.614	7.967	10.817	9.376	9.678	9.018	9.359
5	8.100	6.602	7.241	6.572	8.789	7.666	8.265	7.491	8.421	8.448
6	7.800	8.387	8.841	8.879	8.883	8.607	8.334	8.231	7.633	8.378
7			6.296	7.393	8.673	9.240	9.342	9.131	9.093	9.806
8			8.992	7.902	7.638	8.685	8.378	8.876	8.083	8.552
$\sigma(IP)$ (%)		6.014	12.506	5.288	9.200	5.470	4.895	4.936	5.526	4.470

Measured values are in the left-end column, while the averages of relative errors are shown in the bottom row for each case using different methods.

The last row shows the relative errors for respective methods from the measured data set. Except for RHF-CISD using 6-31G [1] and UHF-MP4 using 3-21G [4], in recent calculations, the relative error from the experiment is of the order of 4–5%. The (worse) results of calculations using the algorism B3LYP, with more elemental basis functions, as 3-21G and 6-31G, were excluded from this table. Our present results derived by B3LYP with 6-31+G** gave one of the most reliable values for IP. After this we used B3LYP with 6-31+G** for our calculations.

Using, the more precise algorithm, higher binding energies (E_B) were often obtained even employing the same basis functions. Fig. 1 shows the binding energy (eV/atom) of neutral clusters (B_n^0) as a function of cluster size, where the results due to B3LYP are compared with previous calculations. With increasing number of composite atoms, the E_B value is anticipated to approach asymptotically to the bulk binding energy. Earlier calculations of E_B [1,4] gave extraordinary high values for B_4^0 and low values for B_5^0, however, those molecular structures did not correspond to the local minimum of PES as mentioned above. Similar calculations of cationic clusters (B_n^+) were performed. Up to present stage, our results are rather close to a calculation performed by Kato et al. [5] and no definite superiority of our calculations has been identified.

3.3. Dissociation energy

Dissociation energies ($\Delta\varepsilon_{nm}$) were obtained using fragmentation patterns Eq. (3) for all B_n^+ clusters.
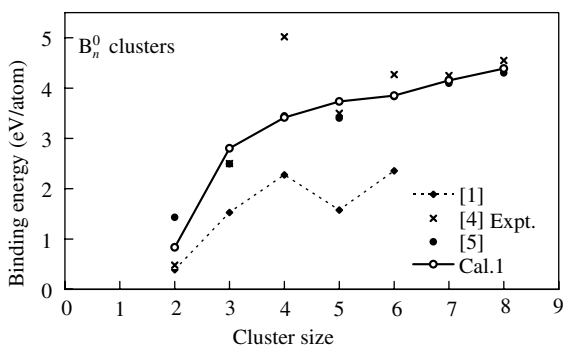

Fig. 1. The binding energy per atom of neutral boron clusters (B_n^0) as a function of the cluster size. Previous calculations are RCISD with 6-31G [1] ($\blacklozenge$), MP4 with 3-21G* [4] ($\times$) and MP4 with 6-31G* [5] ($\bullet$), while present ones (B3YLP with 6-31+G**) are indicated by Calc.1 ($\bigcirc$).
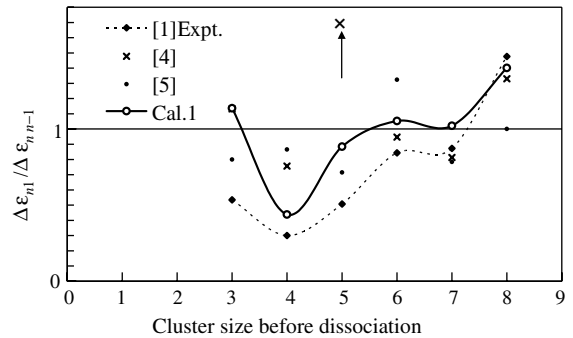

Fig. 2. The ratios of dissociation energies of B^+ dissociation ($\Delta\varepsilon_{n1}$) to B_{n-1}^+ ($\Delta\varepsilon_{nn-1}$) for CID of B_n^+ clusters. The symbols are same with those used in Fig. 1.

The process with the lowest value of $\Delta\varepsilon_{nm}$ should preferentially occur. For all the data for $\Delta\varepsilon_{nm}$, the lowest and the second lowest values $\Delta\varepsilon_{nm}$ were always either $\Delta\varepsilon_{n1}$ or $\Delta\varepsilon_{nn-1}$. This implies a single B^+ or B^0 particle always dissociates, which exactly agrees with the experiment.

Thus far, the accuracy of the absolute value of $\Delta\varepsilon_{nm}$ for each dissociation process has been considered. However, if two dissociation processes are competing with each other as in the present case, it is more significant to compare the ratio of dissociation energies rather than comparing each value correspondingly with measured values. The ratio $\Delta\varepsilon_{n1}$ to $\Delta\varepsilon_{nn-1}$ is shown in Fig. 2. The smaller value in the ordinate denotes a higher possibility of B^+ dissociation to be compared with B^0 dissociation. Comparison with experimental data [1], which is shown by the broken line, increases with cluster size. Previous results [4,5] are denoted by symbols without lines. One '$\times$' symbol [4] located above an arrow indicates an unexpected calculation result [4] where $\Delta\varepsilon_{n1}$ was negative, which corresponds to spontaneous dissociation without any collision. The present result using B3LYP with 6-31+G** is denoted by a solid line. Evidently only our result using B3LYP/6-31+G** reproduces well the dependence of the preferential CID process on the cluster size.

4. Conclusion

We have studied the collision-induced dissociation (CID) of cationic boron clusters (B_n^+) using *ab-initio* molecular orbital calculations based on the density functional method. The experiment to

be referred is CID of B_n^+ ($n \leqslant 8$) colliding with low energy Xe atoms, where only two fragments are produced. Each stable structure of a cationic or neutral cluster corresponded to a corresponding local minimum point of the potential energy surface. This was verified with the help of vibration analysis. Our calculation has improved the accuracy of physical quantities, total energies, ionization potentials, and binding energies. The experimental dissociation dependence on cluster size is closely reproduced. For small boron clusters of B_n^+, B^+ (and B_{n-1}^0) is preferentially fragmented. With increasing the number n of clustered boron atoms, B^0 (and B_{n-1}^+) is increasingly disassociated on collisions.

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