

FRAGMENTATION MECHANISMS FOR MULTIPLY-CHARGED CATIONS

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ABSTRACT

An analysis is presented of the fragmentation of multiply-charged cations $AB^{(n+1)+}$ into $A^{n+} + B^+$ for cases in which the potential energy curve for the fragmentation can be satisfactorily described as arising from an avoided crossing between an attractive state corresponding to $A^{(n+1)+} + B$ and a repulsive state corresponding to $A^{n+} + B^+$. An important quantity is the Gill Δ parameter, given by the difference in ionization energies of A^{n+} and B . A large Δ corresponds to an early transition structure for the fragmentation reaction whereas a small Δ corresponds to a late transition structure. In the latter case, the value of Δ leads readily to estimates of the transition structure bond length and of the kinetic energy released during the fragmentation.

INTRODUCTION

There has been considerable recent theoretical and experimental interest in the gas-phase chemistry of dications.¹ Dications are usually thermodynamically unstable with respect to dissociation into two monocations but significant kinetic stability may result if sufficiently high barriers impede their fragmentation. In order to enable a reliable prediction of the stability of a dication to be made, an accurate theoretical description of this fragmentation process is very important. In this article, we use a recently introduced avoided-crossing model²⁻⁵ to describe dicationic fragmentation and then generalize our treatment to fragmentation of certain more highly charged cations.

METHOD

The calculations referred to in this paper are of the standard ab initio molecular orbital type⁶ with moderately large basis sets and with electron correlation incorporated using Møller-Plesset perturbation theory. Specific details are given in the original papers.²⁻⁵

DISCUSSION

We begin by examining some calculated transition structures for dicationic fragmentation.^{2,3} In the case of symmetric fragmentations, we find that the internuclear separation in the transition structure is typically ~50% greater than that in the equilibrium structure. For example, for the fragmentation of He_2^{2+} , the bond length in the transition structure is 1.15 Å compared with 0.70 Å in the equilibrium structure. In asymmetric fragmentations, on the other hand, the bond length in the transition structure is often 2-3 times or more longer than the equilibrium structure. For example, for the deprotonation of AlH^{2+} , the relevant lengths are 3.59 and 1.65 Å. An even longer bond length (12.5 Å) is found for the transition structure for fragmentation of MgH^{2+} .

Our preferred rationalization^{2,3} for these unusually long transition structure bond lengths begins by considering the potential energy curve along the reaction coordinate for a dissociating AB^{2+} dication as arising from an avoided crossing between a repulsive state which correlates with $\text{A}^+ + \text{B}^+$ and an attractive state which correlates with $\text{A}^{2+} + \text{B}$. The asymptotic energy difference between the two curves (Δ_1) is equal to the difference in adiabatic ionization energies of A^+ and B :

$$\Delta_1 = \text{IE}_a(\text{A}^+) - \text{IE}_a(\text{B}) \quad (1)$$

When Δ_1 is large, the transition structure occurs early and with a shorter bond length (Figure 1). Conversely, we would predict that small Δ_1 values will be associated with late transition structures (Figure 2).

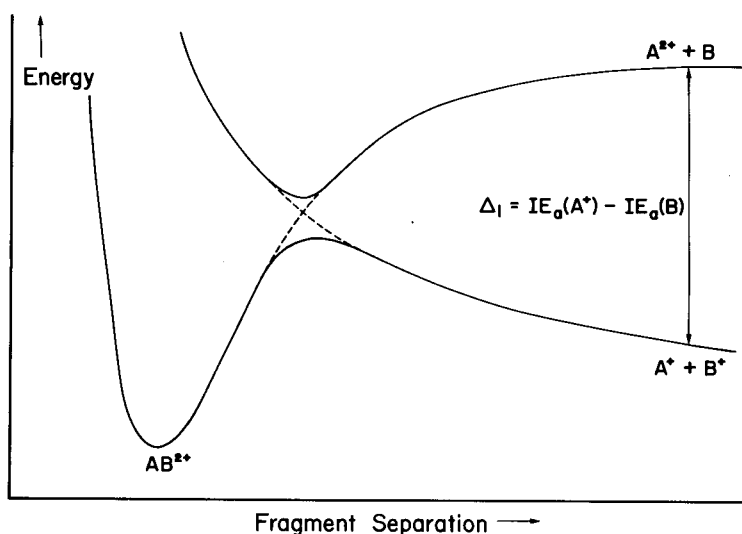


Fig. 1. Schematic potential energy curves describing fragmentation of a general AB^{2+} dication showing avoided crossing between the $\text{A}^{2+} + \text{B}$ and $\text{A}^+ + \text{B}^+$ diabatic potentials when Δ_1 is large.

This Gill Δ parameter is a very useful quantity. For example, it is easy to show that, for sufficiently late transition structures, the bond length in the transition structure is given by²

$$r_{TS} \approx 1/\Delta_1 \quad (2)$$

This formula leads to a transition structure length of 12.40 Å for MgH^{2+} , in close agreement with the directly calculated 12.45 Å. A striking feature is that this formula requires only knowledge of the ionization energies of the fragments formed.

The Δ parameter also provides an estimate of the kinetic energy released in dicationic fragmentations.⁴ The kinetic energy release (T) in the case of a late transition structure is approximately equal to, and is bounded above by, Δ_1 , i.e.

$$T \approx \Delta_1 = IE_a(A^+) - IE_a(B) \quad (3)$$

provided that the coupling between the diabatic $A^{2+} + B$ and $A^+ + B^+$ curves is small and that the electron transfer occurs late, both of which will be the case if Δ_1 is small.

The prediction from equation (3) may be compared⁴ with the observed⁷ kinetic energy release in the case of the SiH^{2+} dication. In this case, Δ_1 is equal to the difference between the second ionization energy of Si (16.35 eV) and the (first) ionization energy of H (13.6 eV). This gives T as approximately equal to (and certainly no greater than) 2.75 eV, which is consistent with the experimental value⁷ of 2.42 eV.

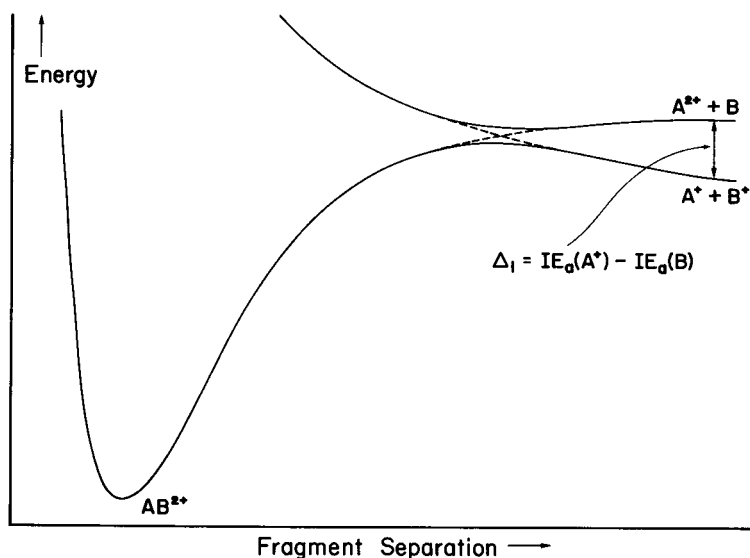


Fig. 2. Schematic potential energy curves describing fragmentation of a general AB^{2+} dication showing avoided crossing between the $A^{2+} + B$ and $A^+ + B^+$ diabatic potentials when Δ_1 is small.

The avoided-crossing model yields detailed information concerning the mechanism of the fragmentation process. In the special case of deprotonation reactions, we find⁴ that such reactions are less straightforward than is often assumed.

In cases where the transition structure for deprotonation occurs late on the reaction pathway, the deprotonation process for AH^{2+} involves (i) homolytic cleavage of the A-H bond to give $A^{\cdot 2+} \cdots H^{\cdot}$; (ii) further stretching of $A^{\cdot 2+} \cdots H^{\cdot}$, now dominated by a (weak) ion-induced-dipole potential with little change in energy; and (iii) a crossing to the $A^+ + H^+$ diabatic potential curve yielding the dissociation products $A^+ + H^+$. This unusual behaviour has important implications regarding the levels of theory required to describe adequately the deprotonation process, and this is discussed in detail elsewhere.⁴

The fragmentation process is further complicated in the case of polyatomic dications where the individual diabatic curves only appear to cross (because they are projections onto the energy-reaction-coordinate plane) while in full coordinate space they do not. The situation is exemplified by the case of deprotonation of $N_2H_6^{2+}$ (Figure 3).

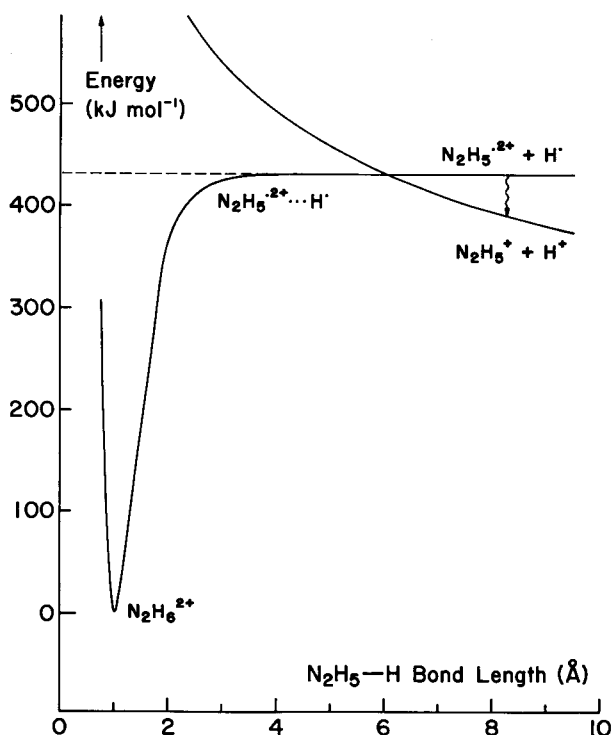


Fig. 3. Potential energy curves describing deprotonation of $N_2H_6^{2+}$. The arrow shows the point at which spontaneous electron transfer can take place from the $N_2H_5^{\cdot 2+} + H^{\cdot}$ potential curve to the $N_2H_5^{+} + H^+$ potential curve.

Again, the fragmentation begins with an early steeply rising section during which the N_2H_5-H bond is homolytically cleaved. Then there is an almost flat plateau due to the very weak (r^{-4}) attraction between $N_2H_5^{2+}$ and H^{\cdot} ; and finally, it becomes energetically feasible for a spontaneous electron transfer to take place, thereby momentarily forming $N_2H_5^+ + H^+$ at the $N_2H_5^{2+} + H^{\cdot}$ geometry. At this point, the dissociation becomes inevitable since the system will rapidly roll down onto the repulsive $N_2H_5^+ + H^+$ path and fragment.

It is easy to show⁴ that the distance (r_{TS}) from the departing proton to the center of charge of A at the transition structure for deprotonation of AH^{2+} is given by

$$r_{TS} \approx 1/(\Delta_1 - \delta) \quad (4)$$

where δ (a positive number) is the difference between the vertical and adiabatic electron affinities of A^{2+} . This is the polyatomic analogue of equation (2).

Finally, we examine⁵ more highly charged ions, specifically $SiHe^{3+}$ and $SiHe^{4+}$.

The $SiHe^{3+}$ trication has a moderately short bond length of 1.670 Å. Although fragmentation to $Si^{2+} + He^+$ is highly exothermic (by 724 kJ mol⁻¹), it is inhibited by an energy barrier of 100 kJ mol⁻¹. The $SiHe^{3+}$ trication is therefore potentially observable in the gas phase. It could perhaps be generated through collision of the Si^{3+} trication with helium.

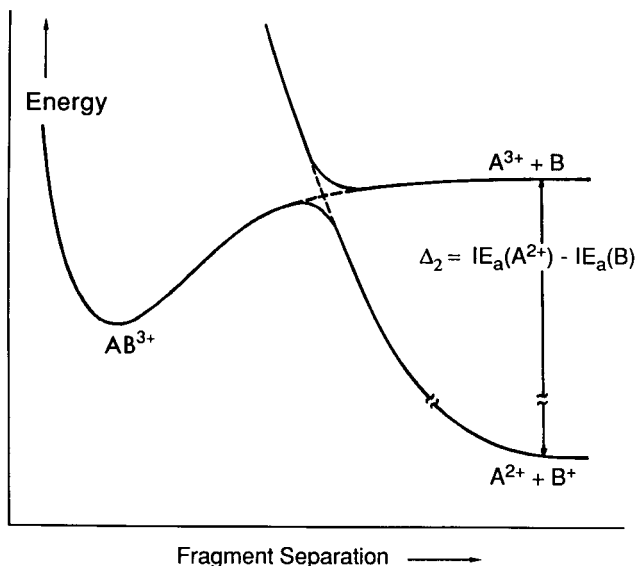


Fig. 4. Schematic potential energy curves describing fragmentation of a general AB^{3+} trication showing avoided crossing between $A^{3+} + B$ and $A^{2+} + B^+$ diabatic potentials.

In cases where we can consider the potential energy curve along the reaction coordinate for a dissociating trication AB^{3+} as arising from an avoided crossing between a repulsive state which correlates with $A^{2+} + B^+$ and an attractive state which correlates with $A^{3+} + B$ (Figure 4), the transition structure bond length is given approximately by⁵

$$r_{TS} \approx 2/\Delta_2 \quad (5)$$

where Δ_2 is the difference between the adiabatic ionization energies of A^{2+} and B. For the case of $SiHe^{3+}$, this equation predicts a transition structure bond length of 3.31 Å, in good agreement with the directly calculated value of 3.29 Å.

For the $SiHe^{4+}$ tetracation, the equilibrium bond length of 1.550 Å is comparable to that of a normal Si-H bond (e.g. 1.481 Å in SiH_4) and has been rationalized⁵ in terms of favorable orbital interactions. Although the exothermicity of fragmentation to $Si^{3+} + He^+$ is enormous (1615 kJ mol⁻¹), the barrier for such a process (76 kJ mol⁻¹) is sufficiently large that we believe that experimental observation will be feasible.

$SiHe^{4+}$, with just two valence electrons, is the smallest stable polyatomic tetracation yet reported.

For a dissociating AB^{4+} tetracation, in cases where the potential energy curve along the reaction coordinate can be considered as arising from an avoided crossing between a repulsive state which correlates with $A^{3+} + B^+$ and an attractive state which correlates with $A^{4+} + B$, the estimated transition structure bond length is given by⁵

$$r_{TS} \approx 3/\Delta_3 \quad (6)$$

where Δ_3 is the difference between the adiabatic ionization energies of A^{3+} and B. For $SiHe^{4+}$, the value of r_{TS} from equation (6) is 2.36 Å compared with the directly calculated value of 2.15 Å.

In general, if the potential energy curve for the fragmentation of a multiply-charged cation $AB^{(n+1)+}$ to give $A^{n+} + B^+$ can be satisfactorily described by an avoided crossing between diabatic curves corresponding to $A^{(n+1)+} + B$ and $A^{n+} + B^+$, the transition structure bond length may be estimated as

$$r_{TS} \approx n/\Delta_n \quad (7)$$

where Δ_n is the difference between the adiabatic ionization energies of A^{n+} and B.

CONCLUDING REMARKS

The important conclusion to emerge from this work is that the avoided-crossing model and the Gill Δ parameter are extremely useful in describing the fragmentation processes of multiply-charged cations.

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