# Simple Models for Describing the Fragmentation Behavior of Multiply Charged Cations

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## Abstract

The potential energy curve describing the fragmentation of a diatomic dication $AB^{2+}$ is considered as arising from an avoided crossing between an attractive diabatic curve (correlating with $A^{2+} + B$) and a repulsive diabatic curve (correlating with $A^+ + B^+$). The simplest avoided-crossing (AC) model neglects diabatic coupling and polarization and leads to useful predictions of the transition structure bond length ($r_{TS}$) and the kinetic energy released ($T$) in fragmentations of dicationic systems in which the difference ($\Delta_1$) between the ionization energies of $A^+$ and B is small. When $\Delta_1$ is not small, it is necessary to include diabatic coupling and polarization in the treatment. The resultant ACDCP (avoided crossing with diabatic coupling and polarization) model provides very satisfactory estimates of $r_{TS}$ and $T$ for both small and large $\Delta_1$. Its implementation requires only atomic ionization energy and polarizability data and comes at virtually no computational cost. Both the AC and ACDCP models are readily generalized to fragmentations of more highly charged cations.

## Introduction

The gas-phase chemistry of dications has attracted considerable recent interest [1]. Although the fragmentation of dications and of more highly charged ions is often highly exothermic, such species may be observable experimentally if the barriers impeding their fragmentation are sufficiently large. In order to enable a reliable prediction of the stability of a multiply charged cation to be made, a satisfactory description of the fragmentation process is therefore very important. In this article we review two avoided-crossing models which we have recently used [2–4] to describe dicationic fragmentation and discuss also their generalization [5, 6] to more highly charged ions.

## The Avoided-crossing Models

Our initial avoided-crossing description of dicationic fragmentation was introduced [2] to rationalize some unusually long bond lengths in the transition structures for certain such processes. Thus, for example, for the deprotonation of $AlH^{2+}$, the bond length in the transition structure is 3.25 Å compared with 1.65 Å in the equilibrium structure [full-valence CI with the 6-311G(MC)$(d,p)$ basis set]. An even longer bond length (12.2 Å) is found for the transition structure for fragmentation of $MgH^{2+}$ [MP4 (full) with the 6-311G(MC)$(d,p)$ basis set]. These results for asymmetric fragmentations may be contrasted with those for symmetric fragmentations, where the internuclear separation in the transition structure is typically only ~50% greater than that

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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.

The model considers the potential energy curve along the reaction coordinate for a dissociating diatomic $AB^{2+}$ dication as arising from an avoided crossing between a weakly attractive state which correlates with $A^{2+} + B$ and a repulsive state which correlates with $A^+ + B^+$. The asymptotic energy difference between the two curves ($\Delta_l$) is equal to the difference in adiabatic ionization energies of $A^+$ and B:

$$\Delta_l = IE_a(A^+) - IE_a(B) \qquad (1)$$

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

The simplest form of the avoided-crossing (AC) model neglects the charge-induced-dipole interaction between $A^{2+}$ and B and also neglects any coupling between the two diabatic states [2]. These assumptions are most nearly valid in cases when $\Delta_l$ is small, and, under such circumstances, the AC model predicts that the bond length in the transition structure is given approximately by

$$r_{TS} \simeq 1/\Delta_l \qquad (2)$$

where $r_{TS}$ and $\Delta_l$ are both in atomic units. This formula leads to a transition structure length of 10.0 Å for $MgH^{\cdot 2+}$, which is likely to be more accurate than the directly calculated 12.2 Å.

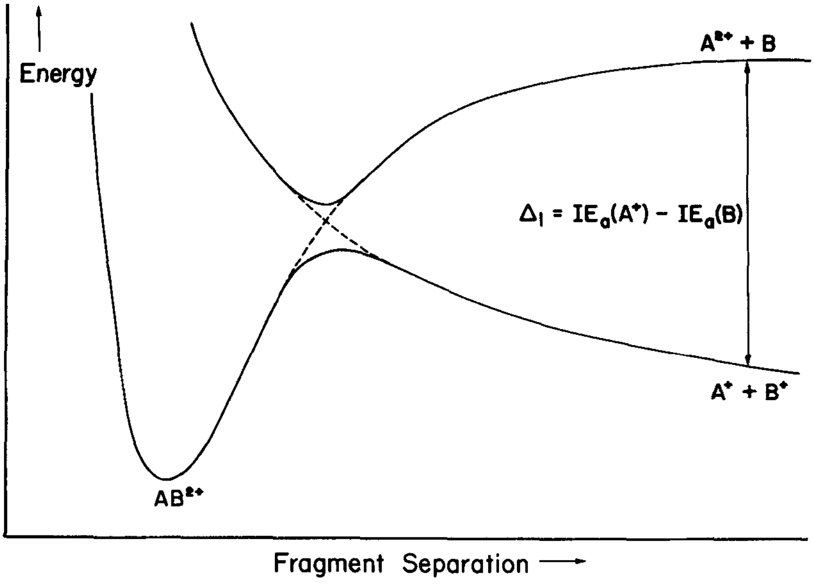

Figure 1. Schematic potential energy curves describing fragmentation of a general $AB^{2+}$ dication showing avoided crossing between the $A^{2+} + B$ and $A^+ + B^+$ diabatic potentials when $\Delta_l$ is large (from Ref. 6).

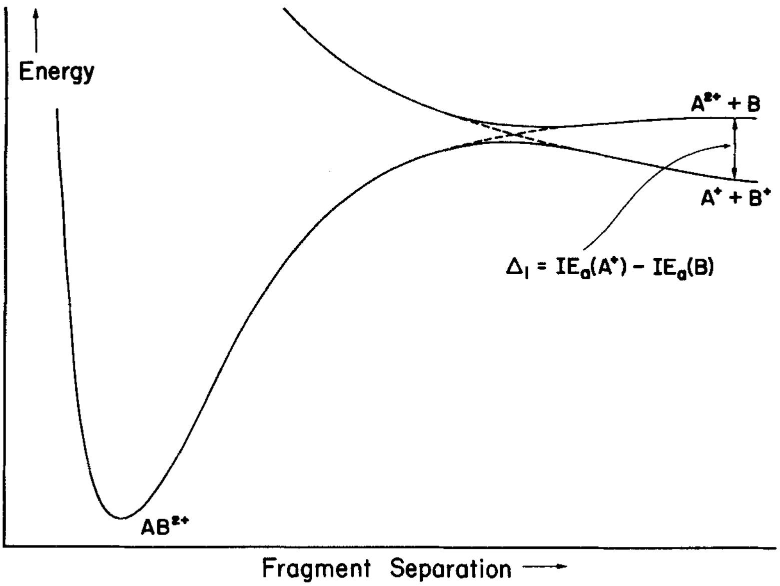

Figure 2. Schematic potential energy curves describing fragmentation of a general $AB^{2+}$ dication showing avoided crossing between the $A^{2+} + B$ and $A^{+} + B^{+}$ diabatic potentials when $\Delta_1$ is small (from Ref. 6).

The AC model also provides an estimate of the kinetic energy released in dicationic fragmentations [3]. The kinetic energy release ($T$) in the case of a late transition structure (i.e., small $\Delta_1$) is approximately equal to, and is bounded above by, $\Delta_1$, i.e.,

$$T \simeq \Delta_1 = IE(A^+) - IE(B) \tag{3}$$

Comparison with an experimentally measured kinetic energy release is possible for the $SiH^{2+}$ dication [7]. In this case, $\Delta_1$ 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). Application of Eq. (3) then indicates that $T$ is approximately equal to (or slightly less than) 2.75 eV, which is consistent with the experimental value of 2.42 eV [7].

The AC model is readily generalized to describe the fragmentation of more highly charged diatomic cations [5, 6]. Thus, if the potential energy curve for the fragmentation of a multiply-charged ion $AB^{(n+1)+}$ to give $A^{n+} + B^{+}$ can be satisfactorily described as 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

$$r_{TS} \simeq n/\Delta_n \tag{4}$$

where $\Delta_n$ is the difference between the adiabatic ionization energies of $A^{n+}$ and B. The kinetic energy release is given approximately by

$$T \simeq \Delta_n = IE(A^{n+}) - IE(B) \tag{5}$$

Examples of the application of the AC model to triply and quadruply charged ions are provided by $SiHe^{3+}$ and $SiHe^{4+}$ [5]. For $SiHe^{3+}$, equation (5) predicts a transition structure bond length of 3.24 Å, in good agreement with the directly calculated value of 3.29 Å. For $SiHe^{4+}$, the predicted value is 2.10 Å compared with the directly calculated value of 2.15 Å.

The simple AC model should be applied only when $\Delta_1$ is small (less than ~2–3 eV). In cases for which $\Delta_1$ is not small, both the polarization attraction between $A^{2+}$ and B and the coupling between the diabatic potential curves may be significant near the crossing point. Consequently, the energy of the $AB^{2+}$ system at the transition structure, while rigorously bounded above by the energies of both diabatic curves, may be so much less than either of them that the approximate formulae (2) and (3) for $r_{TS}$ and $T$ are not useful. In particular, when $\Delta_1$ is not small and the diabatic coupling is large, $T$ will be substantially smaller than $\Delta_1$, and $r_{TS}$ will be substantially larger than $1/\Delta_1$ (Fig. 3).

The more refined form of the avoided-crossing model takes into account both the polarization attraction between $A^{2+}$ and B, and the coupling between the two diabatic potential curves.

In this ACDCP (avoided crossing with diabatic coupling and polarization) model [4] the charge-induced-dipole interaction is taken to be given approximately by the classical expression

$$E_{pol} = -2\alpha_B r^{-4} \tag{6}$$

where $\alpha_B$ is the static electric dipole polarizability of atom B. The magnitude of the diabatic coupling is estimated by constructing a 2 × 2 CI matrix whose diagonal elements [with energies measured relative to $E(A^+) + E(B^+)$] are

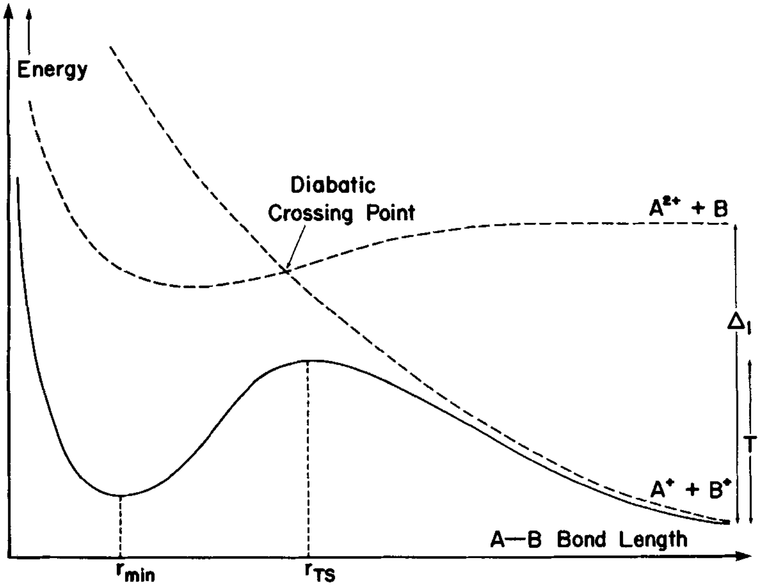

Figure 3. Schematic representation of the diabatic (dashed) and adiabatic (solid) potential energy curves for the ground state of a diatomic $AB^{2+}$ dication. The kinetic energy release $T$ is less than Δ largely because of diabatic coupling and polarization effects (from Ref. 4).

$$H_{11} = 1/r \tag{7}$$

$$H_{22} = \Delta_1 - 2\alpha_B r^{-4} \tag{8}$$

Diagonalization of the CI matrix then leads to the quadratic equation

$$(1 - S_{12}^2)E^2 + (2S_{12}H_{12} - \Delta_1 + 2\alpha_B r^{-4} - 1/r)E + (\Delta_1/r - 2\alpha_B r^{-5} - H_{12}^2) = 0 \tag{9}$$

The off-diagonal element ($H_{12}$) of the CI matrix which appears in Eq. (9) is evaluated using the Wolfsberg–Helmholtz approximation with the standard value from extended Hückel theory taken for the proportionality constant. The CI overlap integral $S_{12}$ is expressed in terms of the atomic orbital overlap integral $S_{AB}$ and evaluated using standard formulae.

The solution of Eq. (9) gives $E(r)$, the energy of $AB^{2+}$ (with inclusion of diabatic coupling and polarization effects) relative to $E(A^+) + E(B^+)$. $E(r)$ may then be maximized with respect to $r$ to obtain the A—B bond length ($r_{TS}$) and the energy ($E_{TS}$) at the transition structure, and the latter quantity may then be equated to the kinetic energy release $T$. It is important to note that the ACDCP estimates of $r_{TS}$ and $T$ require as input only atomic polarizability and ionization energy values.

Representative results obtained with the ACDCP model [4] are presented in Table I. The predicted bond lengths and kinetic energy releases are generally in good agreement with the accurate ab initio and experimental results. The mean absolute error in the predicted $T$ values is roughly 0.5 eV, which, considering the simplicity of the model used, is very encouraging. In contrast, the mean absolute error incurred by using $\Delta_1$ as an estimator of $T$ (i.e., the AC model) is nearly 6 eV. Again, the mean absolute error in the values of $r_{TS}$ predicted by the ACDCP model is 0.23 Å compared with an error of almost 1 Å from the $1/\Delta_1$ approximation. We should emphasize that

TABLE I. Transition structure bond lengths ($r_{TS}$, Å), kinetic energy releases ($T$, eV), and $\Delta_1$ parameters (eV) for dissociating dicationic systems.

| | AC Model | | ACDC Model | | ACDCP Model | | | Reference value[a] | |
|---|---|---|---|---|---|---|---|---|---|
| Dication | $\Delta_1$ | $1/\Delta_1$[b] | $T$ | $r_{TS}$ | $T$ | $r_{TS}$ | $1/T$[a,b] | $T$ | $r_{TS}$ |
| H—Si$^{\cdot 2+}$ | 2.7 | 5.2 | 2.7 | 4.98 | 2.7 | 5.27 | 6.0 | 2.4 | — |
| H—Al$^{2+}$ | 5.2 | 2.8 | 4.7 | 2.82 | 4.5 | 2.94 | 3.8 | 3.8 | 3.248 |
| C—F$^{\cdot 2+}$ | 7.0 | 2.1 | 5.7 | 2.30 | 5.5 | 2.40 | 2.9 | 5.0 | — |
| Be—Be$^{2+}$ | 8.9 | 1.6 | 3.8 | 3.28 | 3.8 | 3.28 | 4.1 | 3.5 | 3.470 |
| H—Cl$^{2+}$ | 10.2 | 1.4 | 6.0 | 2.10 | 5.9 | 2.14 | 2.9 | 5.0 | 2.280 |
| C—Cl$^{\cdot 2+}$ | 11.4 | 1.3 | 5.4 | 2.34 | 5.4 | 2.37 | 2.8 | 5.1 | — |
| H—B$^{2+}$ | 11.5 | 1.2 | 5.7 | 2.17 | 5.7 | 2.18 | 2.4 | 5.9 | 1.801 |
| He—He$^{2+}$ | 29.8 | 0.5 | 9.1 | 1.32 | 9.2 | 1.30 | 1.4 | 10.2 | 1.15 |
| Dev.[c] | 5.7 | 0.9 | 0.6 | 0.27 | 0.5 | 0.23 | 0.5 | | |

Source: Ref. 4.

[a] From accurate calculations or experiment.

[b] Evaluated in atomic units and converted to Angstroms.

[c] Mean absolute deviation from the reference values.

application of the simpler AC model is recommended only when $\Delta_1$ is less than ~2–3 eV, and for only one of the systems in Table I ($SiH^{\cdot 2+}$) is $\Delta_1$ within the required range. We note also that, in the limit of very small $\Delta_1$, the ACDCP and AC results would be expected to coincide.

Also included in Table I are values of $T$ and $r_{TS}$ obtained with the ACDC model [4], which includes diabatic coupling but not polarization. The ACDC and ACDCP results are very similar, but the latter are uniformly slightly closer to the reference values. Because calculations with either model come at virtually no computational cost, we recommend the full ACDCP model for general application.

A formula frequently used by mass spectrometrists to estimate the transition structure bond length of a fragmenting dication is

$$r_{TS} = 1/T \qquad (10)$$

Examination of Figure 3 suggests, however, that, because of diabatic coupling, values of $r_{TS}$ obtained in this manner will consistently be too high. Indeed, we see from Table I that the mean absolute error (0.5 Å) which results from the application of Eq. (10) is roughly twice that of the ACDCP model (0.23 Å).

Finally, we note that generalization of the ACDCP model to fragmentation of a general diatomic multiply charged cation $AB^{(n+1)+}$ (into $A^{n+} + B^{+}$) is quite straightforward. The quadratic equation for $E(r)$ analogous to Eq. (9) is

$$\begin{aligned}(1 - S_{12}^2)E_2 + (2S_{12}H_{12} - \Delta_n + (n+1)^2\alpha_B r^{-4}/2 - n/r)E& \\ + (n\Delta_n/r - n(n+1)^2\alpha_B r^{-5}/2 - H_{12}^2) = 0& \qquad (11)\end{aligned}$$

The values of $r_{TS}$ obtained for $SiHe^{\cdot 3+}$ and $SiHe^{4+}$ using the ACDCP model are 3.10 and 2.36 Å, respectively, compared with the directly calculated values of 3.29 and 2.15 Å.

## Concluding Remarks

The use of the avoided-crossing model without diabatic coupling or polarization (the AC model) leads to approximate expressions for the transition structure bond length ($r_{TS}$) and the kinetic energy released ($T$) in the fragmentation of multiply-charged cations which are useful when $\Delta_n$ is small. Improved estimates of $r_{TS}$ and $T$ may be obtained by introducing diabatic coupling and polarization (leading to the ACDCP model). The refined model is essential when $\Delta_n$ is large. The ACDCP model requires only that ionization energies and static polarizabilities of the relevant atoms be known. The ACDCP procedure is remarkably simple and yet works remarkably well. It should be of value to experimental as well as computational chemists.

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