

THE ACDCP MODEL FOR ESTIMATING THE KINETIC ENERGY RELEASE AND TRANSITION STRUCTURE BOND LENGTH IN THE FRAGMENTATION OF A DIATOMIC DICATION

Peter M.W. GILL and Leo RADOM

Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

Received 8 March 1988; in final form 5 April 1988

A semi-quantitative method is presented for predicting the transition structure bond length and the kinetic energy released as a diatomic dication dissociates into monocation fragments. Our approach, which we term the ACDCP model, involves the introduction of diabatic coupling and polarization effects to an avoided-crossing model previously described. Good agreement is found between the predictions of the new ACDCP model, the results of accurate *ab initio* calculations and experimental results.

1. Introduction

Gas-phase dications have been objects of considerable recent research interest and this has been due, in large part, to advances in experimental design which have enabled mass spectrometric studies of these species to be performed routinely [1]. As a rule, dications are unstable species which dissociate, spontaneously and exothermically, into pairs of monocations,



but they are often experimentally observable because significant barriers can inhibit their fragmentation. The origin and determination of such barriers is a challenging problem to theoreticians and it has been proposed [2,3] that they may be viewed as arising from an avoided crossing between the $A^+ + B^+$ (purely repulsive) and $A^{2+} + B$ (weakly attractive) diabatic potential curves of the AB^{2+} dication (fig. 1). This is a powerful *qualitative* model and may even be *quantitatively* useful when the ionization energies of A^+ and B are comparable, that is, when the Δ parameter [3] defined by

$$\Delta = E(A^{2+}) + E(B) - E(A^+) - E(B^+) \quad (2)$$

is small (less than 2–3 eV). However, in cases for which Δ is not small, the diabatic coupling between the curves may be significant near the crossing point

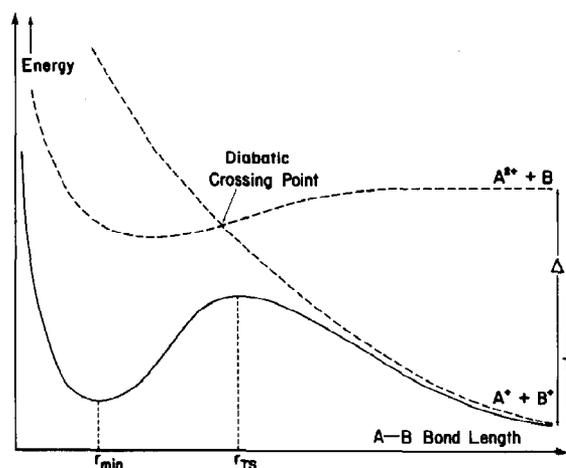


Fig. 1. Schematic representation of the diabatic (dashed) and adiabatic (solid) potential energy curves for the ground state of a diatomic AB^{2+} dication. The kinetic energy release T is less than Δ largely because of diabatic coupling and polarization effects.

and the energy of the AB^{2+} system at the transition structure, while rigorously bounded above by the energies of both diabatic curves, may be substantially lower than either of them. We have previously made the suggestion [4,5] that, if Δ is small, the kinetic energy release T (the difference in energy between the transition structure and the separated fragments) is approximately equal to Δ and that the transition structure bond length r_{TS} is approximately

equal to $1/\Delta$ (r_{TS} and Δ in atomic units). However it is clear that, when Δ is not small and the diabatic coupling is large, T will be substantially smaller than Δ (fig. 1) and r_{TS} will be substantially larger than $1/\Delta$.

An extreme example of such overestimation is provided by the recently observed [6] He_2^{2+} dication, a species for which Δ is particularly large. Although the value of Δ is nearly 30 eV, the kinetic energy release T (according to the very accurate calculations of Yagisawa et al. [7]) is less than 10.2 eV. Clearly, our proposal that $T \approx \Delta$ for systems with small Δ is a poor approximation for the He_2^{2+} dication. In this Letter however, we suggest a refined procedure by which T may be estimated for the fragmentations of diatomic dications, even if Δ is large, and which requires only atomic data as input. This refined procedure also leads to improved estimates of the transition structure bond length.

2. Method and results

Using a modified version [8] of the GAUSSIAN 82 system of programs [9], standard ab initio calculations [10] were carried out for most of the species indicated in table 1 to obtain the geometry and energy of the transition structure involved in each of the fragmentations.

The prototypical dihelium dication He_2^{2+} , which has only two electrons, has been studied by Yagisawa et al. [7] using the very accurate James-Coolidge approach and we have used their results to find an "accurate" transition structure bond length r_{TS} and kinetic energy release T (table 1) for this species.

The diberyllium dication Be_2^{2+} and the boron and aluminium monohydride dications BH^{2+} and AlH^{2+} also have only two valence electrons each and consequently, within the frozen-core approximation, their exact correlation energies (for a given basis set) may be obtained from straightforward CISD calculations. Combining this approach to obtaining frozen-core full CI with the triple-zeta-valence plus d, p-polarization 6-311G(MC)** basis set [11] gives the "accurate" r_{TS} and T values listed in table 1 for these species.

The ground-state triplet hydrogen chloride dication HCl^{2+} is of interest to us as a member of the series of triplet HX^{2+} dications ($\text{X} = \text{halogen}$) which

we considered briefly in ref. [3]. Because it has more than two valence electrons, it is not practical to perform full CI calculations on this system. Nonetheless, by using fourth-order Møller-Plesset perturbation theory in conjunction with the 6-311G(MC)** basis set to find the transition structure bond length and the kinetic energy release (table 1), we believe that we have obtained reliable estimates of these quantities.

Curtiss et al. [12] and Koch et al. [13] have recently measured the kinetic energy releases in the CF^{2+} and CCl^{2+} dications and SiH^{2+} dication, respectively, using mass-analysed ion kinetic energy spectrometry and we have also included these experimental data in table 1.

For comparison, the transition structure bond lengths and kinetic energy releases were calculated for all of the species in table 1 using a simple diabatic coupling plus polarization model which we describe below.

3. Discussion

As two ionized atoms, A^+ and B^+ , approach each other, they initially experience a strong Coulombic repulsion. However, at bonding distances, this is often overcome by even stronger attractive interactions, leading to the appearance of a local minimum on the potential curve. These attractive forces may be traced to a combination of two, quite distinct, electronic effects. The first of these is that the $\text{A}^{2+} + \text{B}$ diabatic curve falls as the A-B bond length r is decreased (fig. 1) because of the enhanced attractive charge-induced-dipole interaction (which increases as r^{-4}). This polarization attraction is electrostatic, and therefore purely classical, in nature which distinguishes it from the second effect - diabatic coupling. The diabatic potential curves "repel" one another to an extent determined by a coupling integral H_{12} which (as we shall see below) decays exponentially with r . Unlike the electrostatic attraction, diabatic coupling is a quantum phenomenon. One consequence of these two effects is that, as r decreases from infinity, the ground-state potential curve, which initially rises with the repulsive $\text{A}^+ + \text{B}^+$ diabatic curve, may subsequently fall as electrostatic and diabatic coupling effects begin to grow rapidly.

Table 1
Transition structure bond lengths (r_{TS} (Å)), kinetic energy releases (T (eV)) and Δ parameters (eV) for dissociating dicationic systems

	AC ^{a)} model		ACDC ^{b)} model		ACDCP ^{c)} model		Accurate calculations ^{d)} or experimental values		
	Δ ^{e)}	$1/\Delta$ ^{f)}	T	r_{TS}	T	r_{TS}	T	r_{TS}	$1/T$ ^{f)}
H-Si ²⁺	2.7	5.2	2.7	4.95	2.7	5.26	2.4 ^{g)}	—	6.0
H-Al ²⁺	5.2	2.8	4.7	2.82	4.5	2.94	3.8	3.248	3.8
C-F ²⁺	7.0	2.1	6.2	2.10	5.9	2.29	5.0 ^{g)}	—	2.9
Be-Be ²⁺	8.9	1.6	3.8	3.28	3.8	3.29	3.5	3.470	4.1
H-Cl ²⁺	10.2	1.4	6.0	2.10	5.9	2.14	5.0	2.280	2.9
C-Cl ²⁺	11.4	1.3	5.4	2.33	5.4	2.37	5.1 ^{g)}	—	2.8
H-B ²⁺	11.5	1.2	5.7	2.17	5.7	2.18	5.9	1.801	2.4
He-He ²⁺	29.8	0.5	9.1	1.32	9.2	1.30	10.2	1.151	1.4

^{a)} "Avoided crossing". ^{b)} "Avoided crossing with diabatic coupling".

^{c)} "Avoided crossing with diabatic coupling and polarization".

^{d)} High-level ab initio results unless otherwise noted, see text. ^{e)} From experimental atomic ionization energies.

^{f)} Evaluated in atomic units and converted to Å. ^{g)} Experimental values, see refs. [12,13].

This is the origin of dicationic stability.

The depth of the well in which a dication resides depends on the magnitudes of both the electrostatic and coupling effects and neither of these may generally be neglected. For example, of the 145 kJ mol⁻¹ well depth in H₂²⁺, approximately 79 kJ mol⁻¹ is due to polarization and 66 kJ mol⁻¹ to diabatic coupling [14]. It is of interest, therefore, to assess the relative importance of these effects in the description of the dissociative region of the fragmentation process, that is, at the transition structure and beyond. Calculation of the transition structure bond length and of the kinetic energy released during fragmentation should provide a useful basis for such an assessment.

We propose that the electrostatic charge-induced-dipole interaction be given approximately by the classical expression

$$E_{\text{pol}} = -2\alpha_B/r^4, \quad (3)$$

where α_B is the static electric dipole polarizability of atom B. We proceed now to describe our approach for estimating the magnitude of the diabatic coupling.

We assume that the A⁺ and B⁺ ions are held together by a single, two-electron bond in the AB²⁺ dication and we focus our attention on formulating a qualitatively correct description of these two electrons because the feature which distinguishes the diabatic A⁺+B⁺ and A²⁺+B curves is, primarily, the distribution of these two electrons. Along one curve, the electrons are localized on the same atom

while, on the other curve, they are covalently shared between both atoms. Suppose that the relevant (normalized) atomic orbitals on A and B are ϕ_i and ϕ_j (although not necessarily respectively). Then the simplest qualitatively correct diabatic spatial wavefunctions for the two electrons on the two diabatic curves are

$$\psi_1(1, 2) = \phi_i(1)\phi_i(2), \quad (4)$$

$$\psi_2(1, 2) = \frac{\phi_i(1)\phi_j(2) + \phi_i(2)\phi_j(1)}{[2(1+S_{AB}^2)]^{1/2}}, \quad (5)$$

where S_{AB} is the overlap between ϕ_i and ϕ_j . We note that, although (4) is not the only simple choice available in the special case of a homonuclear system (i.e. A=B), the use of (4) in all cases ensures that our treatment of homonuclear and heteronuclear diatomics is continuous.

To introduce diabatic coupling, we now allow the (non-orthogonal) diabatic wavefunctions (4) and (5) to mix together via a 2×2 CI. The diagonal elements (H_{11} and H_{22}) of the CI matrix are simply the energies of the diabatic curves which, if we choose henceforth to measure all energies relative to $E(A^+) + E(B^+)$, are $-2\alpha_B/r^4$ and $1/r$ [3]. The off-diagonal element (H_{12}) of the CI matrix is the coupling integral and we propose that the Wolfsberg-Helmholtz approximation [15] be used to estimate it, i.e.

$$H_{12} = \frac{1}{2}KS_{12}(H_{11} + H_{22}). \quad (6)$$

In (6), K is some empirical proportionality constant and S_{12} is the overlap between the diabatic wavefunctions (4) and (5). Thus,

$$S_{12} = \int \phi_i(1) \phi_i(2) \times \frac{\phi_i(1) \phi_j(2) + \phi_i(2) \phi_j(1)}{[2(1+S_{AB}^2)]^{1/2}} d\tau = \frac{2S_{AB}}{[2(1+S_{AB}^2)]^{1/2}}, \quad (7)$$

whence

$$H_{12} = \frac{KS_{AB}(\Delta - 2\alpha_B/r^4 + 1/r)}{[2(1+S_{AB}^2)]^{1/2}}. \quad (8)$$

Finally, diagonalizing the CI matrix gives

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

Solving the quadratic equation (9) gives $E(r)$, the energy of AB^{2+} (with inclusion of diabatic coupling and polarization effects) relative to $E(A^+) + E(B^+)$. Using (7) and (8) to evaluate $E(r)$ numerically requires that the quantities K , α_B , $S_{AB}(r)$ and Δ be known.

We use the value $K=1.75$ suggested, in the context of extended Hückel theory, by Hoffmann [16]. This choice appears to lead to satisfactory agreement with high-level ab initio calculations (vide infra). The static polarizabilities (α values) of all of the main-group elements are known rather accurately ($\pm 2\%$) and are readily available [17]. To evaluate $S_{AB}(r)$, the overlap integral between atomic orbitals, we assume that each orbital is approximated well by a single Slater-type p function (s functions for hydrogen and helium) oriented along the A-B bond. (Although the use of an s function for group I and II metals (e.g. Li and Be) is a more obvious choice, we have found that this is an unnecessary complication which, in any case, scarcely affects the final results.) The overlap integral $S_{AB}(r)$ may then be found by straightforward application of the familiar formulae of Mulliken et al. [18] using standard molecule-optimized atomic ζ values [19]. Finally, Δ may be computed using experimental atomic ionization energies [17].

Given these quantities, $E(r)$ may then be maxi-

mized 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 . In this way, we have obtained the ACDCP (avoided crossing with diabatic coupling and polarization) model results given in table 1^{#1}.

The addition of both diabatic coupling (DC) and polarization (P) corrections to the avoided-crossing (AC) model leads to the ACDCP scheme. Avoided-crossing models of intermediate sophistication, incorporating only diabatic coupling (leading to the ACDC model) or polarization (leading to the ACP model), may also readily be generated. From the comparison of the ACDC results with the corresponding AC and ACDCP values for the eight diatomic dications in table 1, it appears that the polarization correction is much less important (at least, for diatomics) than the correction for diabatic coupling. In turn, this implies that most of the difference between Δ and T is due to diabatic coupling and, therefore, that the diabatic $A^{2+} + B$ curve is almost flat beyond the transition structure (fig. 1). This is probably less true for polyatomic dications (where the principal electrostatic interaction decays as r^{-2}) and for multiply charged cations.

On the whole, the bond lengths and kinetic energy releases predicted by the ACDCP model are in good agreement with the accurate ab initio and experimental results. The mean absolute error in the predicted T values for the eight fragmentations 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 Δ as an estimator of T [3,4] is nearly 6 eV - an order of magnitude larger! Again, the mean absolute error in the values of r_{TS} predicted by the ACDCP model is less than 0.25 Å compared with an error of almost 1 Å from the $1/\Delta$ approximation. We should emphasize that the simple AC model (without diabatic coupling and polarization) is useful only when Δ is less than $\approx 2-3$ eV. The large mean errors obtained with that model in the present paper arise because in only one of the

^{#1} A listing of the complete FORTRAN program (approximately 300 lines) which was used may be obtained from the authors upon request.

systems examined (SiH^{2+}) is Δ within the required range.

A formula routinely used by mass spectrometrists [20] to estimate the transition structure bond length in a fragmenting dication from measured values of the kinetic energy release is

$$r_{\text{TS}} \approx 1/T. \quad (10)$$

This gives substantially better results than the $1/\Delta$ estimates (table 1) when Δ is not small. However, because of the effects of diabatic coupling (fig. 1), we believe that the values of r_{TS} derived from (10) using accurate values of T will be consistently too high. Indeed, the mean absolute error (0.5 Å) which results from the application of (10) to the five species in table 1 for which accurate r_{TS} values are known is roughly *twice* that of the ACDCP estimates of r_{TS} (0.25 Å).

The success of the ACDCP model in estimating r_{TS} and T and, in particular, the fact that it appears to yield better r_{TS} values than the $1/T$ approximation has prompted us to make ACDCP predictions for the sets of AH^{2+} and AHe^{2+} dications ($\text{A} = \text{Be}$ to Ne , Mg to Ar). The values of r_{TS} and T obtained in this manner are listed in table 2 for comparison with existing and prospective experimental data. We stress that these predictions come at virtually no computational cost and require as input only atomic data.

The data in table 2 not only provide quantitative estimates of r_{TS} and T for systems for which the fragmentation curves have the qualitative form of that in fig. 1 but also serve to indicate whether a particular dication may not exist or, on the other hand, whether it might be thermodynamically stable. Thus, although the ACDCP model will always yield a value of r_{TS} , small values of r_{TS} should be interpreted as suggesting a small, or nonexistent, potential well. In addition, a negative value of Δ indicates that the $\text{A}^{2+} + \text{B}$ diabatic curve always lies below the $\text{A}^+ + \text{B}^+$ diabatic curve and, therefore, that the AB^{2+} dication is thermodynamically stable.

In summary, the use of the avoided-crossing model without diabatic coupling or polarization [2,3] leads to the approximations [3–5]

$$r_{\text{TS}} \approx 1/\Delta, \quad (11a)$$

$$T \approx \Delta. \quad (11b)$$

Table 2

Calculated transition structure bond lengths (r_{TS} (Å)) and kinetic energy releases (T (eV)) from the ACDCP ^{a)} model for ground state AH^{2+} and AHe^{2+} dications

A	AH^{2+} systems			AHe^{2+} systems		
	r_{TS} ^{b)}	T	Δ ^{c)}	r_{TS} ^{b)}	T	Δ ^{c)}
Be	3.2	4.1	4.6	–	–	d)
B	2.2	5.7	11.5	25.7	0.6	0.6
C	2.0	6.2	10.8	–	–	d)
N	1.8	6.9	16.0	2.9	4.9	5.0
O	1.5	7.6	21.5	1.7	7.8	10.5
F	1.4	8.5	21.4	1.6	8.1	10.4
Ne	1.2	9.6	27.4	1.3	9.7	16.4
Mg	10.0	1.4	1.4	–	–	d)
Al	2.9	4.5	5.2	–	–	d)
Si	5.3	2.7	2.7	–	–	d)
P	2.6	5.0	6.1	–	–	d)
S	2.2	5.8	9.7	–	–	d)
Cl	2.1	5.9	10.2	–	–	d)
Ar	1.9	6.5	14.0	4.7	3.0	3.0

^{a)} "Avoided crossing with diabatic coupling and polarization".

^{b)} A small predicted value of r_{TS} suggests that the species may not be experimentally observable (see text).

^{c)} From experimental atomic ionization energies.

^{d)} The Δ parameter is negative implying that there is no transition structure for the fragmentation of this (thermodynamically stable) dication, i.e. there is no reverse activation energy.

These are both useful when Δ is small. By introducing diabatic coupling and polarization (leading to the ACDCP model) we have shown how improved estimates of r_{TS} and T may be obtained. The refined model is essential when Δ is large.

4. Conclusion

In this Letter, we have proposed a refinement of the avoided-crossing model for the fragmentation of diatomic dications which enables reasonable a priori predictions of the associated kinetic energy release and transition structure bond length to be made regardless of the size of the Δ parameter. This new ACDCP model requires only that the first and second ionization energies and the static polarizabilities of the relevant atoms be known. The procedure works remarkably well and, since kinetic energy releases are comparatively easy to measure, it should be of value to experimental, as well as computational, chemists.

Acknowledgement

We thank Professor J.A. Pople and Mr. J.R. Ischtwan for very helpful discussions regarding this manuscript. We also gratefully acknowledge a generous allocation of time on the Fujitsu VP-100 of the Australian National University Supercomputer Facility.

References

- [1] W. Koch, F. Maquin, D. Stahl and H. Schwarz, *Chimia* 39 (1985) 376;
W. Koch and H. Schwarz, in: *Structure/reactivity and thermochemistry of ions*, eds. S.G. Lias and P. Ausloos (Reidel, Dordrecht, 1987), and references therein.
- [2] F.H. Dorman and J.D. Morrison, *J. Chem. Phys.* 35 (1961) 575.
- [3] P.M.W. Gill and L. Radom, *Chem. Phys. Letters* 136 (1987) 294.
- [4] L. Radom, P.M.W. Gill and M.W. Wong, in: *The structure of small molecules and ions*, eds. R. Naaman and Z. Vager (Plenum Press, New York, 1988).
- [5] P.M.W. Gill and L. Radom, to be published.
- [6] M. Guilhaus, A.G. Brenton, J.H. Beynon, M. Rabrenovic and P. von R. Schleyer, *J. Phys. B* 17 (1984) L605.
- [7] H. Yagisawa, H. Sato and T. Watanabe, *Phys. Rev. A* 16 (1977) 1352.
- [8] J. Baker, R.H. Nobes, D. Poppinger and M.W. Wong, unpublished;
J. Baker, *J. Comput. Chem.* 7 (1986) 385.
- [9] J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Raghavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fluder and J.A. Pople, *GAUSSIAN 82*, Carnegie-Mellon University, Pittsburgh.
- [10] W.J. Hehre, L. Radom, P. von R. Schleyer and J.A. Pople, *Ab initio molecular orbital theory* (Wiley, New York, 1986).
- [11] M.W. Wong, P.M.W. Gill, R.H. Nobes and L. Radom, to be published.
- [12] J.M. Curtiss, A.G. Brenton and R.K. Boyd, *Chem. Phys.* 116 (1987) 241.
- [13] W. Koch, G. Frenking, H. Schwarz, F. Maquin and D. Stahl, *J. Chem. Soc. Perkin Trans. II* (1986) 757.
- [14] P.M.W. Gill and L. Radom, to be published.
- [15] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* 20 (1952) 837.
- [16] R. Hoffmann, *J. Chem. Phys.* 39 (1963) 1397.
- [17] R.C. Weast, ed., *Handbook of chemistry and physics*, 67th Ed. (CRC Press, Boca Raton, 1986).
- [18] R.S. Mulliken, C.A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.* 17 (1949) 1248.
- [19] R. Poirier, R. Kari and I.G. Csizmadia, eds., *Handbook of Gaussian basis sets* (Elsevier, Amsterdam, 1985).
- [20] J.H. Beynon and A.E. Fontaine, *Chem. Commun.* (1966) 717;
R.G. Cooks, J.H. Beynon, R.M. Caprioli and G.R. Lester, *Metastable ions* (Plenum Press, New York, 1978).