

Quantitative Valence-bond Computations of Curve Crossing Diagrams for a Gas-phase S_N2 Reaction: $F^- + CH_3F \longrightarrow FCH_3 + F^-$

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A quantitative curve crossing diagram for the identity S_N2 reaction, $F^- + CH_3F \longrightarrow FCH_3 + F^-$, is computed with the multistructure VB method, at the PS-31 + G^* level with a basis set of double-zeta plus polarization quality with pseudo-potentials for the core electrons and additional diffuse functions. The VB value for the central barrier is *ca.* 11.3 kcal mol⁻¹, in agreement with a recent estimate based on experimental data (reference 9) and with most modern MO computations followed by correlation corrections (reference 7*b,d*). Because of the low energy of the triple ion structure, $F^-CH_3 + F^-$, the variational curves can be generated all the way to the crossing point, but beyond it the variational procedure does not terminate in the charge-transfer state despite the natural correlation of the VB structures to this state. The relationship between the natural correlation and the variational VB procedure is discussed. It is shown that this feature of the variational procedure does not affect its ability to provide the key curve crossing quantities *at their variational values*. These quantities are, in turn, found to follow the trends of the qualitative model. The vertical charge-transfer energy gap is large (241.8 kcal mol⁻¹). The height of the crossing point relative to the ion-dipole cluster is 37.25 kcal mol⁻¹ (*ca.* 15% of the gap). The resonance energy of the transition state is 25.9 kcal mol⁻¹. The relationship between the barrier and the curve crossing quantities is discussed by comparison to the hydride exchange reaction, $H^- + CH_3H \longrightarrow HCH_3 + H^-$. It is shown that the relative barriers reflect the interplay between the charge-transfer energy gap and the curvature which determines the height of the crossing point relative to the gap. This behaviour is in good agreement with the predictions of the qualitative curve crossing model. The significance of the curvature factor is shown to be related to the characteristic structure-reactivity coefficients of the reaction (*e.g.*, the Brønsted coefficient).

The curve crossing diagram has been advocated in recent years as a general paradigm for the conceptualization of chemical reactivity.¹⁻⁴ The principal yardstick, against which the utility and the validity of the model have been tested, is the S_N2 reaction.^{1*a,c,2*} For an identity S_N2 reaction, the diagram of which is shown in Fig. 1, three curve crossing quantities are required for a discussion of reactivity patterns.

The first quantity is the gap (G_0) which corresponds to the vertical charge-transfer excitation from the anion X^- to the valence $\sigma^*(C-X)$ orbital of the CH_3-X molecule.^{1*a,3a*} The second quantity is the curvature factor (f) which determines the fraction of the gap that enters under the crossing point. Since, for quite a few gas-phase reactions, both the crossing point and the barrier^{2,4} may be lower than the separate reactants, it is customary to refer these quantities to the geometry of the ion-dipole cluster, and thereby avoid the less aesthetic alternative of using negative values for barriers and heights of crossing points. Thus, one is concerned with the height of the crossing point fG_C and with the 'central barrier', ΔE_C^\ddagger , and both refer to the reactant cluster C_R in Fig. 1.⁴ The third curve crossing quantity in Fig. 1 is the avoided crossing interaction, B , which is also the quantum mechanical resonance energy (QMRE) of the transition state.^{3*a,5*} The central barrier thus becomes eqn. (1).

$$\Delta E_C^\ddagger = fG_C - B \quad (1)$$

By relying on these three quantities it has proved possible to

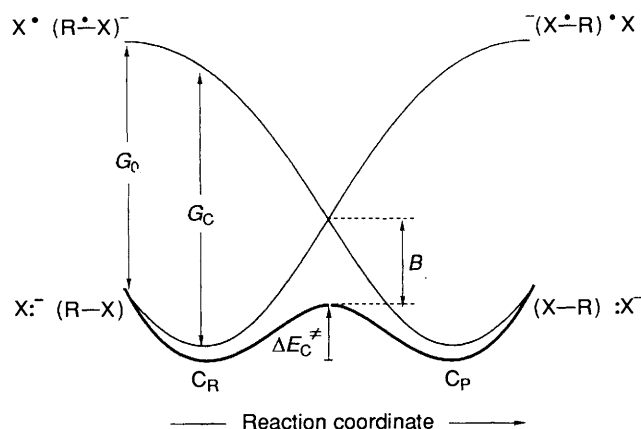


Fig. 1 A qualitative curve crossing diagram for the identity S_N2 process
 $X^- + RX \longrightarrow XR + X^-$

pattern computational and experimental structure-reactivity data in a coherent manner.^{1*a,c,2*} This effort has been largely qualitative and based on a number of simplifying assumptions which, no matter how useful, still require quantitative verifications which, in turn, will also serve to refine and articulate the original ideas.

Recently, it has been shown³ that curve crossing diagrams can indeed be computed at the *ab initio* level using multistructure valence bond (VB) computations.⁶ For the hydride exchange S_N2 reaction ($X = H$ in Fig. 1)^{3*a*} the computations provide curve crossing quantities in accord with the qualitative expectations, and a potential-energy barrier in agreement with MO computations followed by correlation corrections. While

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Table 1 Optimized geometries^a for the critical species in the reaction:

Parameter	Species		
	CH ₃ F	F _l /CH ₃ F _r (C _R) ^b	(F ₁ ...CH ₃ ...F _r) ⁻ , TS ^b
r(C-H)/Å	1.0799	1.0715	1.0597
r(C-F _r)/Å	1.3743	1.4429	1.8832
r(C-F _l)/Å	—	2.5927	1.8832
θ(HCF)/deg	108.38	107.26	90.00

^a These are PS-31G*(D) values; PS = pseudopotential. ^b C_R = reactant cluster. TS = Transition state.

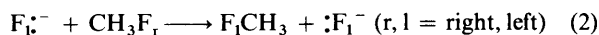
Table 2 Ion-dipole stabilization energy, ΔE_{id}, and central barrier, ΔE_c[‡] for the reaction:

Quantity	This study		Wolfe and Kim ^c		
	SCF ^b	VB ^b	SCF ^c	MP2 ^c	MP4 ^d
ΔE _{id} ^a	-12.93	-16.68	-12.84	-15.31	-14.19
ΔE _c ^{‡a}	17.66	11.35	18.54	12.93	10.14

^a In kcal mol⁻¹. 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹. ^b Refers to the geometries in Table 1. The basis set is PS-31G*(D). ^c Results from reference 7(d) with full geometry optimization at the respective level. ^d MP4//MP2/6-31 + G* results from reference 7(d).

this is pleasing, a more extensive and general appraisal of the model as well as of the computational methodology is deemed necessary, and this is the general aim of this paper.

The target reaction in this manuscript is the fluoride exchange, eqn. (2), which itself has been a subject of numerous



ab initio MO computations⁷ and was one of the first S_N2 reactions to be assigned an experimental central barrier.⁸ More recently, the experimental central barrier has been judged, both by theory^{7b,d,k} and by new experiments,⁹ to be too high. Thus the height of this particular central barrier and its estimate by VB theory are also of interest. Accordingly this paper presents VB calculations of the barrier for the reaction (2), and shows how the barrier arises by avoided crossing of the corresponding Lewis-type curves of reactants and products. The curve crossing quantities are calculated and compared with those in other reactions^{3a,10} and with qualitative predictions.^{1,2,4}

Theoretical Methods and Calculations

Methods.—The multi-structure VB method used here is based on the same principles as other multi-structure VB methods,^{11,12} and has been discussed before^{3,6} in great detail. What follows here is a brief reminder of the main points of the method. An essential feature is the use of localized AOs or fragment orbitals with no delocalization tails on other atoms or fragments. In this respect, the method preserves the relationship between the VB function and the chemical structure as regards the assignment of the electrons to specific atoms. The wavefunction and energy of a VB structure is computed by a variational mixing of an elementary VB function, built with Hartree-Fock optimized orbitals, with all the Brillouin states¹³ that represent the same VB structure, in terms of charge-type and spin-pairing mode, as the elementary VB function, and

which are generated from this elementary VB function by intra-fragment monoexcitations. As has been shown,^{6d,e} the resulting set of VB functions are equivalent, to a first approximation, to a single VB structure whose orbitals are optimized^{6e} with respect to their size, hybridization and polarization. When the VB procedure involves different VB structure-types, the result is equivalent to a non-orthogonal MCSCF calculation of a VB wavefunction reduced to its set of constituent VB structures, in which both the coefficients and orbitals would be optimized simultaneously;^{6e} each such structure has its own specific set of orbitals, optimized in the presence of the other VB structures, but different from one structure to another.^{3a}

In the present work the dimension of the non-orthogonal CI is reduced by a preliminary selection of Brillouin states in double zeta basis set. All unimportant Brillouin states are discarded, provided that the total energy rise due to this simplification does not exceed 2 kcal mol⁻¹ in the absolute energy of the diabatic wavefunction and 1 kcal mol⁻¹ in the adiabatic one. The VB procedure was restricted to the 'active' bonds, which are the two interchanging C-F bonds, eqn. (2), and to their respective constituent orbitals. The rest of the bonds (C-H bonds of the methyl moiety) and lone pairs are treated at the Hartree-Fock level with allowance for the C-H bonds to relax and polarize by single excitations (*e.g.*, mixing of σσ* configurations). The various VB functions were generated exactly as described before for the H⁻ exchange reaction.

Calculations.—The non-orthogonal CI among the VB functions was performed by means of a program written by Lefour and Flament.¹⁴ The MONSTERGAUSS program¹⁵ was used for the initial Hartree-Fock optimization of the fragment and atomic orbitals as well as for the SCF geometry optimizations of the various critical structures for the target reaction: reactants, cluster and transition state. The geometry optimizations and VB calculations were carried out with the PS-31G basis set,¹⁶ which involves pseudo-potentials for the cores of C and F, complemented with polarization functions on C and F and diffuse functions on F. Accordingly we refer to this basis set hereafter as PS-31G*(D). The exponents of the polarization and diffuse functions are taken from the standard 6-13 + G* basis set. In addition, some of the curve crossing quantities were also calculated with the 6-31G basis set to check their potential basis set dependence. The charge-transfer states in the VB diagram were computed as explained recently,^{3a} without the diffuse orbitals. This is in keeping with the original ideas that the excited states involve valence-type anion radicals. Inclusion of diffuse orbitals in this calculation is indeed irrelevant because these radical anions are unbound with respect to a loss of an electron.¹⁷

Results

Geometries of the Critical Points and Energetics of the Adiabatic Potential-energy Profile.—The geometric details of the three critical points are collected in Table 1. The CH₃F parameters are in good agreement with experiment.¹⁸ The cluster geometry is comparable to the results of basis sets of at least double-zeta quality, although our distance between the anion and the molecule (2.59 Å) is shorter in comparison with more extended basis sets, such as those used by Vetter and Zulicke^{7b} and by Dedieu and Veillard^{7c} (2.74 Å and *ca.* 3 Å, respectively). The C...F bond length in the transition state ranges between *ca.* 1.8 and 1.9 Å for basis sets of double-zeta plus polarization quality.^{7b-k} Our result of 1.88 Å is longer than those of the 6-31G* and 6.31++G** basis sets^{7j,k} and somewhat closer to the values obtained by means of the more extended basis sets.^{7b}

Table 2 shows the ion-dipole stabilization energies and

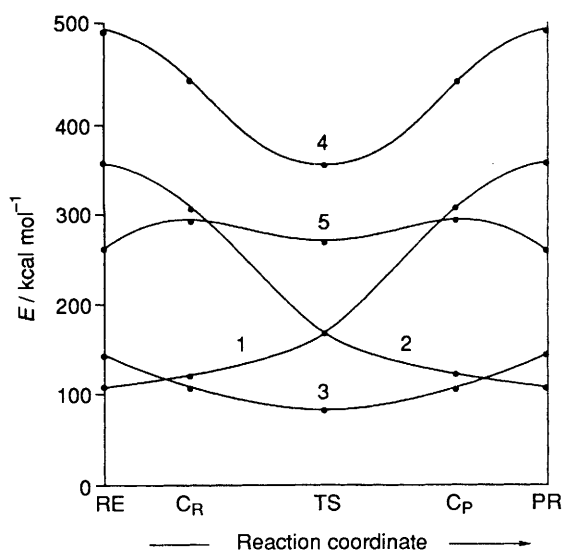


Fig. 2 The energetic behaviour of the VB configurations 1–5 along the reaction coordinate. The geometries of reactants, reactant cluster, transition state, product cluster and products are referred to as RE, TS, C_R, C_P and PR, respectively.

barriers computed at the SCF and VB levels with the PS-31G*(D) basis set with pseudo-potential. Recent results by Wolfe and Kim^{7d} which refer to all-electron calculations in the 6-31 + G* basis set provide a good basis for comparison, and are tabulated in Table 2 alongside our results. Our VB results have comparable accuracy to the results of Wolfe and Kim with respect to the absolute magnitudes of the barrier and the ion-dipole stabilization energy, as well as with respect to the effect of correlation correction on the SCF barrier. Indeed all other recent results indicate that the correlated barrier is lower than the SCF barrier by 3–6 kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹).^{7b,d,e,k} While there are no definitive values for either the barrier or the ion-dipole energy, the most extensive calculations so far, by Vetter and Zulficke,^{7b} lead to a central barrier of 15.5–17.1 kcal mol⁻¹ and ion-dipole energies of -(13.1–13.3) kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹). Thus the VB and the MO + correlation barriers all agree with the recent experimental estimate of the barrier by DePuy *et al.*⁹ and indicate that the first experimental assignment, by Pellerite and Brauman^{8a} of 26.2 kcal mol⁻¹ for the barrier, is too high by 9–16 kcal mol⁻¹. In conclusion, the VB method takes proper account of the effect of correlation on the central barrier and the ion-dipole complexation energy.

Discussion

(a) *VB Configuration and their Energies along the Reaction Coordinate.*—The VB structures which mix to generate the reaction profile for the target reaction are shown below in structures 1–7 which describe the possible ways to distribute the four electrons, of the anion F:⁻ and the C–F bond, in those orbitals which participate in the bond interchange, as well as in the ‘inactive’ orbitals of the CH₃ moiety. Structures 1 and 2 correspond to the covalent Heitler–London (HL) configurations which describe the spin-pairing in the C–F bonds of reactants and products. Structure 3 is the most stable triple-ion configuration with a positive charge on the central methyl moiety (R) flanked by two negative charges on the fluorines. Structure 4 known as the ‘long bond structure’,^{1a,c,f,2,3a} possesses spin-pairing of the odd electrons on the two fluorines and a negative charge on the methyl moiety. Structure 5 describes the delocalization of the negative charge into the

inactive σ* orbitals of the C–H bonds of the methyl group. This latter structure was found to be the key^{3c,d} for the stability of SiH₅⁻, but is not expected to play a significant role in S_N2 reactions on carbon, especially when the entering- and leaving-groups are electronegative atoms as in eqn. (2).^{3c,d,10} The remaining structures 6 and 7, with a negative charge placed on the methyl moiety and with an unfavourable arrangement of the charges, are expected to be of very high energy and will not concern us at the qualitative level.

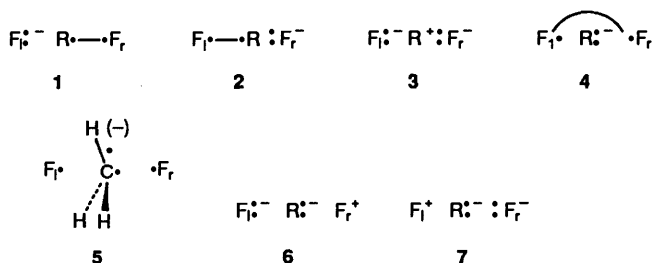
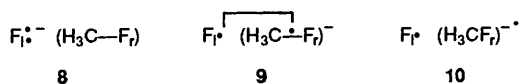


Fig. 2 is a plot of the VB-computed energy of structures 1–5 at the five critical points of the reaction coordinate: reactants and products, the respective ion-dipole clusters and the transition state. It is seen that the two HL structures, 1 and 2, intersect along the reaction coordinate thereby forming the spine of the curve crossing diagram.^{1b} Since the ground states of reactants and products and the respective clusters are produced from the mixing patterns of the HL configurations,^{6c} then the crossing of these two configurations is also the root cause of the barrier. We can therefore focus on the spine of the HL curves and dress this spine with the other configurations, 3–7 and thereby generate the two state-anchored curves, which by avoided crossing will become a diagram analogous to Fig. 1.^{1,3a} Already at this point we note that each excited HL anchor point is related to the ground-state configuration below it by a single electron transfer, from the F:⁻ anion to the F atom in the molecule, and this forms the basis for the charge-transfer character of the excited states in the diagram.

(b) *Construction of a Two-curve Diagram by VB Mixing.*—The ground states of reactants and products result from the mixing of the HL structures with the triple ion structure 3. This mixing generates the ground states with the conventional Lewis electron-pair C–F bonds in the CH₃–F molecule, as depicted schematically in 8 for the reactants. As the anions approach the molecule from infinity, the two ground states will be stabilized primarily by ion-dipole/induced dipole interactions leading thereby to the corresponding clusters C_R and C_P, respectively; F:⁻/CH₃–F, and F₁–CH₃/F:⁻. The wave functions of the clusters are expected to be dominated, much like in the separated reactants and products, by VB mixing of the corresponding HL configuration with the triple ion configuration. For example, C_R will arise primarily from the mixing of HL structure 1 with the ionic structure 3, while the configurations 2 and 4–7, which are much higher in energy at this geometry, are assumed to mix in to a negligible extent. At this stage of the VB mixing we have generated two curves which are anchored in the Lewis ground states and at the two HL excited configurations.^{1f} As such each one of the curves describes a homolytic dissociation of a Lewis bond along the S_N2 reaction coordinate, e.g., F:⁻ + (CH₃–F) → (F:⁻·CH₃) + ·F.



To complete the excited states of the diagram we have now to mix structures 4 and 5 into the excited HL points of the above

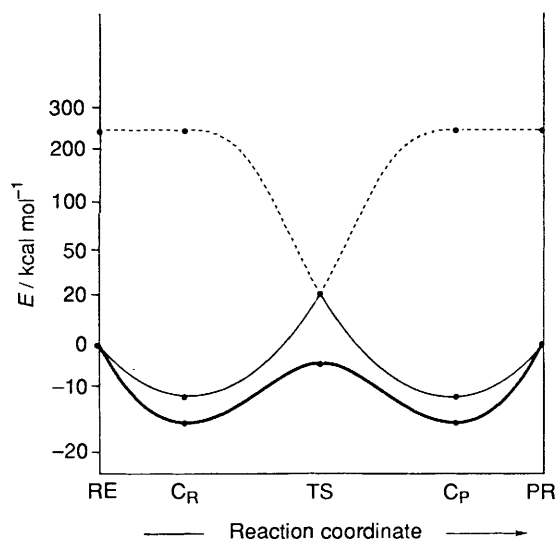
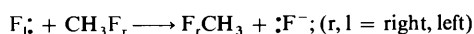


Fig. 3 The VB-computed curve crossing diagram for the reaction



The dashed lines indicate the natural correlation of the diabatic curves beyond the crossing point. The dark line indicates the adiabatic reaction profile resulting from avoided crossing. The reaction coordinate is defined in Fig. 2. The energy coordinate is represented for convenience as a logarithmic scale.

curves. Consider for example, the reactant extreme in Fig. 2 where the excited HL configuration is 2. By mixing into 2 some of the configuration 4 there will result a charge-transfer state which possesses three electrons in the C-F linkage, as shown in 9. Two of the three electrons in this linkage occupy the $\sigma(\text{C-F})$ orbital while the third electron resides in the $\sigma^*(\text{C-F})$ orbital.^{1a,c,f,2} Further mixing of 9 with structure 5 will also delocalize the third electron into the $\sigma^*(\text{CH}_3)$ orbital of the appropriate symmetry (a_1 symmetry)^{3a} and thereby generating the charge-transfer state 10 with a delocalized anion radical (CH_3F_r)⁻. At the reactant end the charge-transfer state, 10, will be dominated by configuration 5 which is the lowest in energy, while at the cluster geometry the charge-transfer state will be more like 9, because of the intrinsic stabilization of 2 by the spin-pairing and the strong mixing of 2 with 4 as opposed to the weak mixing with 5.* In any event, the excited anchor point at the reactant extreme will be related to the ground state below it by a charge-transfer excitation from the anion F_r^- to the molecule CH_3F_r . Completely analogous arguments apply for the product extreme of the reaction coordinate where the excited anchor point will be the charge-transfer state which corresponds to a charge-transfer excitation from F_r^- to the F_rCH_3 .

These are the VB mixing patterns responsible for the identity of the anchor states in the qualitative curve crossing diagram in Fig. 1. Anywhere else along the reaction coordinate, each one of

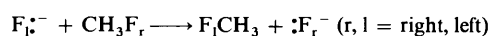
the curves will be made of a mixture of one of the HL structures mixed with 3-7. Each such wavefunction represents a single bonding situation (reactant- or product-like) the dominant character of which will be the mixture of a HL configuration with the ionic structure 3, much like a Lewis electron-pair structure. We therefore refer to the individual curves as 'Lewis curves'.

(c) *Natural VB Correlations and the Quantitative Two-curve Diagram.*—The above discussion shows that the origins of the state correlation in Fig. 1 is the intersection of the spin-paired HL forms of reactants and products. Since all S_N2 reactions share this same feature their curve crossing diagrams should be similar to each other and to Fig. 1. In our recent paper on the H^- exchange S_N2 reaction^{3a} it was shown that it is possible to compute the individual Lewis curves variationally throughout the reaction coordinate. This was done by carrying out two separate VB calculations in the two configuration subsets which are defined by reactant's and product's bonding situations. The reactant's bonding situation is defined by the mixture of HL configuration 1 with all other configurations except for HL configuration 2 which, in turn, defines the basis for the product's bonding situation. While this variational calculation went smoothly and completely for the H^- exchange, applying the same procedure to the target reaction will generate the appropriate variational curves up to the crossing point, but not beyond this point.

Let us elucidate the quantitative problem by discussing the procedure for generating the curve that starts out at the reactant ground state. The variational procedure utilizes for this purpose the subset of VB configurations which constitute the reactant's bonding situation namely; HL (1) with 3-7. As discussed above, at the reactant extreme structure 1 mixes only with 3 and the variational wavefunction will be dominated by 1 which is the lowest in energy of the two configurations. Near the cluster geometry, the variational curve is still made predominantly from 1 and 3, but now the ionic structure constitutes the major character of the curve, and this will persist as we proceed along the reaction coordinate. Past the crossing point, the ionic structure continues to be the lowest and its energy gap with the higher-lying HL (1) gradually increases at the same time that the overlap between these two configurations gradually diminishes.* Similar behaviour applies to the overlap of 3 with all the other configurations in the bonding set.* Consequently the mixing of 3 with HL (1) and the other configurations in the set becomes weaker and weaker, until we reach the product extreme where the variational curve becomes purely structure 3. Exactly the same situation is expected whenever the ionic configuration 3 lies below the excited charge-transfer anchor points. In all these cases, because of the gradual vanishing of the 3-1 mixing, the variational procedure will not trace the natural VB correlation, ground state \longrightarrow charge transfer state, but, rather, will lead beyond the crossing point to an artificial excited state made of pure structure 3. The natural correlation can be retrieved, however, by use of Malrieu's method of projection of an MO-CI wavefunction onto the VB configurations, although the variational character of the crossing point will be lost in the process.¹⁹

While the variational procedure does not continuously connect the ground to the charge-transfer states, it still provides the essential curve crossing quantities in line with the qualitative analysis. This is illustrated in Fig. 3 which shows the computed curves and their avoided crossing which leads to the adiabatic energy profile, along the same reaction coordinate as in Fig. 2. Also shown in Fig. 3 are the natural anchor points of the curves, the two valence charge-transfer states which are computed separately. The curves are shown by solid lines up to the crossing point, and beyond it they are connected to the charge-

* The mixing rules in approximate VB theory are discussed in reference 1(c). According to rule a [p. 171 in reference 1(d)] two configurations will mix in proportion to the overlap of the two orbitals which differ by a single electron occupation. Thus, 2 mixes with 5 in proportion to the overlap of the 2p AO of F_r with the $\sigma^*(\text{CH}_3)$ orbital. Owing to the poor overlap capability of the latter orbital [references 3(c), (d) and 10] this mixing will be weak even if the energy gap between the configurations is small. On the other hand, 2 and 4 mix strongly because the mixing is proportional to the overlap of 2p AO of F_r with the axial 2p AO of the CH_3 moiety. The mixing of 3 with 1 is proportional to the overlap of 2p(C) and 2p(F_r). This mixing becomes zero at the product extreme where the $C \cdots F_r$ distance is infinity. The mixing patterns of 3 with all the other configurations can be deduced simply from the mixing rule.

Table 3 Curve crossing quantities^a for the reaction:

G_0	G_c	f	B
241.8	253.9	0.1467 ^c	25.9
184–229 ^b	(257.7)	0.1445	26.9 ^d 23.4 ^e

^a G and B are in kcal mol⁻¹ (1 kcal mol = 4.184 kJ mol⁻¹). f is dimensionless. ^b Experimental values from reference 17(b), (c). ^c This value refers to the gap of 253.9 kcal mol⁻¹ from the diabatic Lewis curve. The other value refers to the gap of 257.7 kcal mol⁻¹. ^d This value refers to curves generated from structures 1–3 only. ^e This value was obtained with the 6-31G basis set.

transfer states by dashed lines, which in turn convey the idea that these portions are not computed but drawn in accord with the natural VB correlations.

In this manner, the computations in Fig. 3 provide all the ingredients of eqn. (1): the charge-transfer energy gap, the height of the crossing point and the QMRE quantity, B . Thus, despite the incomplete correlation, there is still an advantage in the variational procedure because it provides, in fact, the essential curve crossing quantities at their variational values. Especially important in this sense is the QMRE quantity which, when computed variationally, provides the resonance energy of the delocalized transition state relative to the most stable localized-bonding situations at the crossing point. Let us discuss now the diagram and its curve crossing quantities and relate them to other computed values.^{3a,10}

(d) *Energetics of the Curve Crossing Diagram.*—Let us discuss some of the properties of the Lewis curves and the adiabatic profile by reference to Fig. 3 and Table 3.

The gap factor. The first quantity in Table 3 is the charge-transfer energy gap at the separated reactants. As already mentioned, this gap is obtained by calculating a valence charge-transfer state devoid of diffuse orbitals, such that the molecule possesses a negative electron affinity. The closest physical analogue of the anion radicals in these charge-transfer states are the unbound temporary anions which are detected as scattering states in the electron-transmission (ETS) experiment.¹⁷ Indeed Heinrich *et al.*²⁰ have concluded that only basis sets which are devoid of diffuse orbitals can reproduce the trends in the experimental ETS electron affinities. If we stick with this analogy we can obtain the experimental estimate of the charge-transfer energy gap by use of the ionization potential²¹ of F_1^- and the electron affinity^{17b,c} of CH_3F . The so estimated experimental gap is shown alongside the computed G_0 value in Table 3. The uncertainty in the experimental gap derives from the uncertainty in the assignment of the experimental electron affinity of CH_3F . Using the experimental assignment of Giordan *et al.*^{17b} the resulting gap is 229 kcal mol⁻¹; in very close agreement with the VB computations, while using the theoretical assessment of the experimental value by Lindholm *et al.*^{17c} leads to the smaller gap which is quite different from the VB value. However, a rough correspondence does exist especially if we look at trends in the VB-computed values and compare them with trends in the corresponding experimental values or the qualitatively estimated values,^{1a,2} e.g., for the present reaction and the H^- exchange reaction.

The second quantity in Table 3 is the charge-transfer energy gap at the geometry of the cluster, G_c . The second G_c value refers to the gap between the adiabatic state of the cluster and the charge-transfer state, while the first value refers to the quantity from the diabatic Lewis curve. In the original qualitative model^{1a,22} it was assumed that the charge-transfer

stabilization of the ion-dipole cluster is negligible and that consequently the diabatic curve and the adiabatic potential will approximately coincide at the cluster geometry, much as they do at the reactant geometry. As can be seen, from Fig. 3 and the G_c values in Table 3, the adiabatic profile is 3.8 kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹) more stable than the diabatic Lewis curves at the cluster geometry. This stabilization is due to the mixing of the charge-transfer configurations (9, 10) into the Lewis structure (8), at the cluster geometry. This mixing depends on the $F_1 \cdots C$ distance between the anion and the molecule and is expected to be basis-set dependent much as the $F_1 \cdots C$ distance itself. Thus it is expected that with more extended basis sets, where this distance is longer than ours, the mixing will be smaller and the diabatic and adiabatic curves will also be near coincidence at the cluster geometry. In any event, the 3.8 kcal mol⁻¹ difference in the gaps is only 1.5% of the gap itself and will lead to a negligible error (ca. 0.5 kcal mol⁻¹) in the use of eqn. (1).

A more significant deviation is the difference between the gap value at the reactant and the cluster geometries, amounting to 13–16 kcal mol⁻¹ (5–6% of the gap size). In the qualitative applications, it was assumed that the ion-dipole stabilization energy of the cluster will be compensated by the lowering of the charge-transfer state, 9, due to stabilization by spin-pairing of the odd electrons. Using this assumption one can use the readily available G_0 values instead of the G_c values for estimating the central barrier in eqn. (1). While this assumption does not hold here the barrier error caused by using this assumption will be of the order of 1.7 kcal mol⁻¹ which is still satisfactory for semiquantitative purposes. Future applications should reveal whether this deviation is a peculiarity of the F^- exchange reaction or whether the assumption breaks down systematically.

The f factor. According to the qualitative model the f factor should be small because of the localized nature of the charge-transfer state of type 9 and the added effect of the dominant mixing of the triple-ion configuration along the reaction coordinate.^{1a} As may be seen in Table 3 the computed f value is indeed very small. In order to test the origins of the small computed f we took advantage of the fact that the VB method allows an explicit analysis of the effect of the various configurations on the f factor.

For the HL curves the f_{HL} value is 0.31 which is close to the corresponding value for the H^-/CH_4 reaction ($f_{HL} = 0.33$). Upon addition of the triplet-ion structure 3, the corresponding f values should decrease, because the mixing of 3 into the HL curves makes them more concave and as a result a smaller fraction of the gap enters under the crossing point. This effect is moderate in the H^-/CH_4 reaction where the triple-ion configuration is high-lying and the resulting f value decreases accordingly in a moderate fashion to 0.27. In contrast, the triple-ion configuration for the F^-/CH_3F reaction is very low-lying and accordingly it lowers the f factor drastically to 0.12.

We turn now to consider the effect of the remaining configurations on the f factor. In the qualitative model,^{1a,f} the other configurations serve to delocalize the odd electron of the anion radical and to weaken thereby the bond coupling between the two odd electrons in the charge-transfer states. The more delocalized the odd electron in the anion radical the less concave the curves become and the f factor concomitantly increases. In the H^-/CH_4 reaction, addition of the remaining configurations generates the $(CH_4)^-$ anion radical where the odd electron is extensively delocalized over all the identical C–H linkages. Accordingly f increases from 0.27, its value in the localized anion radical, and becomes 0.42.^{3a} On the other hand, in the F^-/CH_3F reaction, mixing of the remaining configurations generates a significantly less delocalized anion

Table 4 Central barriers and curve crossing quantities for identity S_N2 reactions

Reaction	ΔE_c^\ddagger	G	f	fG	B
F^-/CH_3F	11.35	253.9	~0.15	37.25	25.9
H^-/CH_4	56.80	174.0	0.42	57.7	15.9

^a All values except for f are in kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹).

radical, and the corresponding f value is raised from 0.12 only to ca. 0.15 as recorded in Table 3.

It follows that the f factor is a measure of the VB mixing and the bond coupling along the reaction coordinate. S_N2 reactants whose charge-transfer states are delocalized (localized) will lead to a large (small) f value, while reactants which possess a low-lying (high-lying) $X^-R^+X^-$ configuration will have a small (large) f value. As we have noted in the qualitative applications of the model,^{1a,23} the f factor is a measure of the *sensitivity of a reaction series to a change* e.g., of basicity of the nucleophile. Thus, substrates with a low-lying R^+ configuration will be less sensitive to substituent change, and this will be manifested in small Brønsted coefficients, small Swain–Scott parameters and small Hammett ρ values. Such observations, of small structure–reactivity coefficients, have been made in recent years by Kirby *et al.*²⁴ and by Jencks *et al.*²⁵ for the S_N2 reactions of CH_3OCH_2X derivatives, for which the R^+ structure is expected to be dominant and indeed proved to be so.

The B factor. The B values in Table 3 are all quite close to one another. Firstly, from the second B value, it is seen that this quantity is determined mainly by the Lewis structures, and therefore resembles a classical resonance energy between the Lewis forms of the reactants and products. Secondly, this quantity is seen to be very slightly basis-set dependent, much like the case for the H^-/CH_4 reaction. This is a satisfactory feature of a property which provides the QMRE of the transition state.⁵

The value of B is seen to be small in comparison with the charge-transfer energy gap. This is important since the adiabatic profile remains close to the diabatic curves; a fact which allows the adiabatic state to be considered in terms of properties of the diabatic curves. The B value of 26 kcal mol⁻¹ is larger than the qualitatively used value of 14 kcal mol⁻¹. Thus, while the value for the H^-/CH_4 reaction was close to the qualitative estimate in the present reaction the deviation from the qualitative value is significant. As we shall immediately show, however, this does not in any way affect the discussion of trends according to the model.

The central barrier: discussion of an archetypal trend. Table 4 compares the curve crossing quantities of the F^-/CH_3F reaction with those of the H^-/CH_4 reaction, in line with the barrier expression in eqn. (1). As can be seen, the gap for F^- exchange is much larger than for H^- exchange and despite this relationship the former reaction possesses a much smaller central barrier. The reason for that is seen to lie entirely in the ratios between the height of the crossing point and the corresponding charge-transfer energy gaps. These ratios are the f factors which provide a measure of the curvature or concavity of the curves, which in turn is determined by the strength of the bond coupling and the configuration mixing along the reaction coordinate. This was precisely the conclusion of the qualitative model which is now corroborated by the quantitative calculations. Thus, while B is not a constant it is still a 'passive variable', and the trends in the relative barriers of identity S_N2 reactions are determined by the interplay of the charge-transfer energy gap and the curvature factor which is a measure of the bond-coupling and the configuration mixing along the reaction coordinate.^{1,2,3a}

Conclusions

This paper presents a quantitative construction of a curve crossing diagram for the identity S_N2 reaction, $F^- + CH_3F \rightarrow FCH_3 + F^-$, using the multistructure VB method.⁶ The VB value for the central barrier is ca. 11.3 kcal mol⁻¹, in agreement with the recent experimental estimate⁹ and with estimates of modern MO computations followed by correlation corrections.⁷ The most direct comparison is with the results of Wolfe and Kim^{7d} which show that the accuracy of the VB method is comparable to Hartree–Fock calculations followed by a good correlation treatment.

Because of the low energy of the triple-ion structure, $F^-CH_3^+F^-$, the variational curves can be generated all the way to the crossing point, but beyond it the variational procedure terminates in the pure triple-ion configuration instead of the charge-transfer state as would be required from the natural correlation of the VB structures to this state.* The relationship between the natural correlation and the variational VB procedure is discussed. It is shown that this feature of the variational procedure does not affect its ability to provide the key curve crossing quantities at their variational values. The relationship between the barrier and the curve crossing quantities is discussed by comparison with the hydride exchange reaction, $H^- + CH_3H \rightarrow HCH_3 + H^-$. It is shown that the relative barriers reflect the interplay between the charge-transfer energy gap and the curvature factor which determines the height of the crossing point relative to the gap. This behaviour is in good agreement with the predictions of the qualitative curve crossing model. The significance of the curvature factor is discussed with reference to the characteristic structure–reactivity coefficients of the reaction (e.g., the Brønsted coefficient).

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* For the term natural correlation see reference 26. A discussion of the same type of the diagram using natural correlation with increased valence structures is discussed in reference 27.

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