

Non-adiabatic Reactions

1. Overview

Theoretical explanations of the chemical processes leading to the generation of a mass spectrum are usually given in terms of the characteristics of the potential energy surface of the ground electronic state of the molecular ion. Modern quantum chemistry programs that automatically look for so-called stationary points are available. This means that they are able to determine either minima of the potential energy surface, which determine ionic structures, or saddle points, which determine activation barriers.

However, there exist additional features of the potential energy surfaces that are considered less frequently and yet have mechanistic importance. These are crossings and avoided crossings between potential energy surfaces characterizing different electronic states of the molecular ion. For some reactions there exist regions where two potential energy surfaces intersect or are separated by a small energy gap, of the order of a vibrational quantum. The Born–Oppenheimer approximation then breaks down and so-called nonadiabatic interactions can occur (1–6). This means that in these regions the nuclear motion is no longer determined by the shape of the ground state potential energy surface. Furthermore, the motion of the nuclei induces a transfer of population between the two approaching surfaces, which can have important chemical consequences. Reactions that involve a jump in the electronic structure are termed nonadiabatic.

2. Adiabatic and Diabatic States

Consider an avoided crossing along a given nuclear coordinate R , i.e., a region where two potential energy curves become close without crossing each other. The essence of the problem is due to the fact that, in the neighborhood of such an avoided crossing, the electronic structure is a sensitive function of the nuclear geometry. Let us denote by Ψ_1 and Ψ_2 the electronic wave functions obtained by solving the Schrödinger equation with a quantum chemical program. (In technical terms, they are eigenfunctions of the Born–Oppenheimer electronic Hamiltonian.) Generally, it is observed that, as shown in Fig. 1, they correspond to a particular electronic configuration for geometries located on one side of an avoided crossing and to another configuration on the other side of the crossing. For example, on the left-hand side of a crossing one might have $\Psi_1 = \Phi_1$ and $\Psi_2 = \Phi_2$, whereas on the right-hand side one would find $\Psi_1 = \Phi_2$ and $\Psi_2 = -\Phi_1$. (The reader should not be disturbed by the presence of the minus sign. It is required by the mathematical property of orthogonality of the wave functions.)

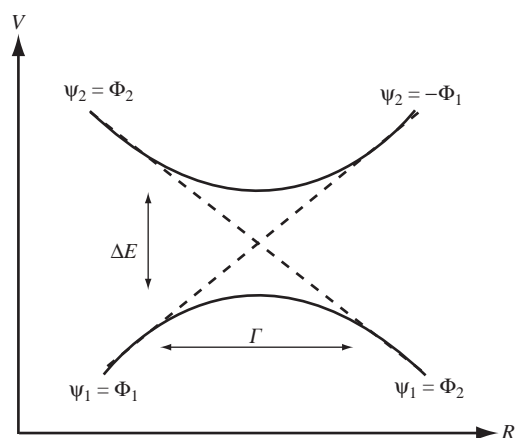


Figure 1

Avoided crossing leading to nonadiabatic interaction. The adiabatic potential energy curves are drawn as full lines; the diabatic curves are represented by dashed lines. ΔE is the smallest energy gap between the two interacting adiabatic surfaces and Γ is the width of the coupling region. Ψ_1 and Ψ_2 denote the adiabatic wave functions whereas Φ_1 and Φ_2 are the diabatic functions.

States Φ_1 and Φ_2 denote two simple electronic structures (described either in the molecular orbital or in the valence bond languages). For example, Φ_1 might characterize a valence electronic state whereas Φ_2 refers to a Rydberg state. Alternatively, Φ_1 might describe an electronic state where an electron has been removed from the π shell (as in the $C_6H_6^+$ ion) whereas Φ_2 refers to a state where an electron has been extracted from the σ shell (as in the pair $C_6H_5^+ + H$, see below). In the intermediate region, where the avoided crossing takes place, the wave functions gradually change their character, i.e., they undergo a smooth conversion from Φ_1 to Φ_2 or vice versa, as the nonadiabatic coupling region is crossed. In this so-called nonadiabatic coupling region the two wave functions Ψ_1 and Ψ_2 can be expressed as a linear combination of both Φ_1 and Φ_2 .

The actual solutions of the Schrödinger equation, Ψ_1 and Ψ_2 are termed adiabatic states. States Φ_1 and Φ_2 , however, are not solutions of this equation in the nonadiabatic coupling region. They are referred to as diabatic states and defined as states that correspond to a particular electronic configuration.

Note that in the coupling region the ground state wave function Ψ_1 is necessarily a mixture of (at least) two configurations (i.e., Φ_1 and Φ_2). Therefore, a usual quantum chemistry program, which is based on the self-consistent field (SCF) approximation approach, cannot be expected to lead to converged results. Much more complicated programs based on the multiconfigurational SCF (MCSCF) or configuration interaction (CI) approaches are necessary to

generate sensible results in this case. However, the simple SCF approximation retains its usefulness, because it often provides a good approximation to diabatic states (see *Theory (Energies and Potential Energy Surfaces): Theoretical Methods*).

3. Connection with Chemical Reactivity

Energies can be associated with each of the four states Ψ_1 , Φ_1 , Ψ_2 , and Φ_2 . The potential energy curves associated with diabatic states Φ_1 and Φ_2 (represented by dashed lines in Fig. 1) can cross. However, potential energy curves associated with adiabatic states Ψ_1 and Ψ_2 (represented by solid lines in Fig. 1) avoid each other. For this reason, the diagram is said to describe an avoided crossing.

In this connection, it is particularly important to consider the magnitude of the smallest energy gap between the two interacting adiabatic surfaces, denoted ΔE in Fig. 1. Nonadiabatic interaction can be important when ΔE is small (of the order of a vibrational quantum). If ΔE is much larger (say, of the order of 1 eV or more), then the Born–Oppenheimer approximation remains valid, and the nonadiabatic coupling is usually neglected. Therefore, it is essential to distinguish between cases where the splitting between adiabatic curves is large vs. cases where the splitting is small. However, it will be seen in the section devoted to transition probabilities that the Massey parameter provides a much better criterion than these orders of magnitude guidelines.

Figure 1 immediately suggests that nonadiabatic interactions often generate barriers in the potential energy surface and therefore may account for the existence of transition states. As explained elsewhere (7) curve crossings are now considered to provide a basis for understanding chemical reactivity. They are a natural development of Woodward and Hoffmann's landmark contribution on reaction symmetry (8).

Another kind of nonadiabatic interaction is also possible. Avoided crossings are said to result from the so-called noncrossing rule. This expression summarizes a general theorem of quantum mechanics, which says that the eigenvalues of a Hamiltonian cannot cross if they have the same group-theoretical symmetry. However, the theorem is valid only for Hamiltonians that parametrically depend on a single degree of freedom. It automatically applies to diatomic molecules, but its application to polyatomic molecules is more subtle. Avoided crossings, described in Fig. 1, are still possible but, in addition, a more complicated kind of nonadiabatic interaction, giving rise to so-called conical intersections, is often observed.

Consider, for example, the well-known reaction $C_6H_6^+ \rightarrow C_6H_5^+ + H$ (where both the benzene ion and the phenyl ring adopt a cyclic structure). This

reaction must necessarily involve a nonadiabatic step. The reason is that the positive hole is localized in the π shell of the $C_6H_6^+$ ion, whereas the $C_6H_5^+$ ion has a fully occupied π shell (9). The nonadiabatic nature of the reaction is clearly displayed when the symmetry of the electronic states is specified: $C_6H_6^+ [(\sigma_{CH})^2 \pi^5] (^2B_1) \rightarrow C_6H_5^+ [\pi^6] (^1A_1) + H [1s_H] (^2S)$. In this new kind of nonadiabatic interaction, the adiabatic curves can cross, because they belong to different symmetry species (2B_1 and 2A_1 in the present case). However, distinction between 2B_1 and 2A_1 states is possible only if the molecular ion retains C_{2v} symmetry along its dissociation pathway. Now, a full potential energy surface necessarily considers all geometries of the nuclear framework, symmetrical or not. For less symmetrical nuclear configurations, the symmetry species of both states is the same and the surfaces avoid each other. Altogether, they cross for some nuclear geometries and repel for others. The net result is referred to as a conical intersection, depicted in Fig. 2 and studied in more detail below.

In summary, nonadiabatic interaction opens up new vistas on chemical reactivity. Chemical reactions are often described as a stream of trajectories in a $2f$ -dimensional phase space, consisting of f nuclear degrees of freedom plus f associated momenta. Reaction mechanisms are determined by so-called bottlenecks that restrain the reactive flux in phase space. In many cases these bottlenecks are accounted for by energy barriers, which lead to conventional saddle points. However, in some cases, especially frequent in photochemistry and mass spectrometry, bottlenecks can also result from more complicated kinds of nonadiabatic interaction (see *Theory (Reactions): Statistical Theories in Mass Spectrometry*).

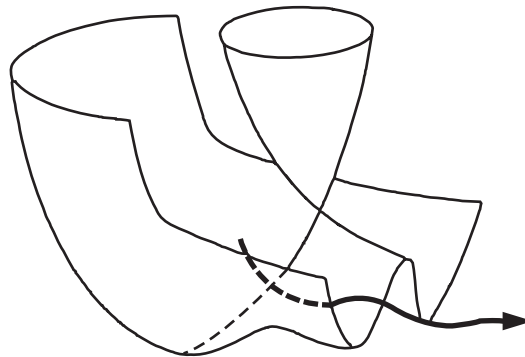


Figure 2
Conical intersection: the two adiabatic potential energy surfaces present the topology of a double cone jointed at an apex. Thick line: low-energy adiabatic nuclear trajectory around the cone.

4. Nonadiabatic Transition Probability

Radiationless transitions between two adiabatic potential energy surfaces depend on factors other than the magnitude of ΔE alone. They are especially probable under the following circumstances: (i) the surfaces are close in energy (ΔE is small); (ii) the nuclear velocities are large; and (iii) the change in the electronic structure as the molecular geometry is changed is abrupt. This is easily understood. If the nuclei are moving sufficiently slowly and if, furthermore, the rearrangement of the electronic configuration takes place gradually over a large range of internuclear distances, then the electrons have ample time to readjust (i.e., the electronic wave function Ψ_1 has time enough to switch from Φ_1 to Φ_2). The adiabatic description is then appropriate. By contrast, if the nuclei move rapidly in a range where the nature of the electronic wave function changes abruptly, there is not enough time for the electrons to rearrange to a new configuration and the diabatic description is preferable.

These propensities are summarized in the dimensionless Massey parameter ξ (1-4), which provides a much better criterion for the existence and efficiency of nonadiabatic interaction than the value of ΔE alone:

$$\xi = \frac{\Delta E \Gamma}{\hbar v}$$

where v denotes the nuclear velocity and Γ is the width of the coupling region, i.e., the range of internuclear distances over which the physical nature of the electronic states changes (Fig. 1). A small value of Γ indicates that the electronic wave functions depend sensitively on the nuclear geometry. Slowly moving nuclei in a range where the adiabatic potential energy surfaces are well separated and change their electronic configuration only gradually bring about a value of the Massey parameter much larger than unity. The reaction is then perfectly well described by the ground state potential energy surface calculated by a quantum chemical program.

However, the state of affairs is radically different in the opposite situation, i.e., when the Massey parameter is small with respect to unity. Under these circumstances, the chemical process is governed by the propensity to remain in the same electronic configuration throughout. The diabatic (crossing) potential energy surfaces then provide a much more reliable description of the nuclear motion. In other words, jumps between adiabatic potential energy surfaces can take place. These jumps are called nonadiabatic transitions.

The Massey parameter is also widely used in collision theory (1, 2). Γ is now defined as the range of the interaction potential between the two colliders. Two limiting cases are considered, depending on

whether the transit through the nonadiabatic region is fast or slow. The corresponding regimes are denoted "sudden" when $\xi \ll 1$ and "adiabatic" when $\xi \gg 1$. (The sudden regime corresponds to the diabatic description.) However, the value of Γ is not related to the distance of closest approach between the projectile and the ion, as occasionally found in the literature.

The Landau-Zener equation expresses this propensity in a quantitative way. The probability P of hopping from one adiabatic surface to the other is given by

$$P = \exp[-(\pi\xi/4)]$$

It should be noted, however, that this equation is no longer valid when the nuclear velocity v is too small (1, 10). Nonadiabatic transitions can occur even when v is small provided that ΔE and Γ are also small enough. For this reason, the Landau-Zener equation should be applied with care to study reactions close to their energy threshold. However, a slightly more complicated equation of quantum mechanical origin is available to deal with these cases, at least when the nonadiabatic coupling is weak (1, 10).

For polyatomic molecular ions there exists an extension of the RRKM theory that can be applied to the calculation of microcanonical rate constants of nonadiabatic reactions (11-17).

5. Classification

In all cases, the two diabatic surfaces are, to a first approximation, planes that cross along a straight line, called the seam (Fig. 3). However, one has to distinguish among three cases, depending on whether

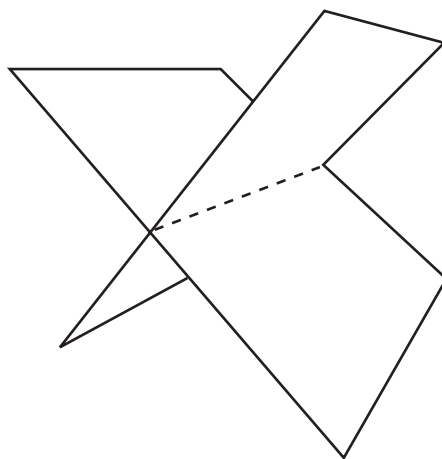


Figure 3
Two diabatic surfaces crossing along the seam (represented by a dotted line).

the nonadiabatic interaction results from the spin-orbit coupling (case (a)) or from the dynamical interaction of the electrons with the nuclei (cases (b1) and (b2)).

5.1 Case (a): Spin-forbidden Reactions

The total spin angular momentum is not the same in the initial and in the final states of the reaction. The two diabatic surfaces that cross are characterized by different multiplicities. For open-shell molecular ions, Φ_1 could be a doublet whereas Φ_2 is a quartet. For closed-shell systems (e.g., the phenyl ion $C_6H_5^+$), the ground state Φ_1 is a singlet state whereas Φ_2 is a triplet (9). Higher multiplicities are commonly observed in organometallic chemistry (18–20).

The diabatic states Φ_1 and Φ_2 are then coupled by the spin-orbit interaction (10). Let H_{12} denote the magnitude of the coupling. Then, the quantity ΔE that appears in the Massey parameter and in the Landau-Zener formula is equal to $2H_{12}$.

The spin-orbit interaction is weak for atoms in the first row of the periodic table, but increases roughly as the second or third power of the atomic number of the heaviest atom present in the molecular ion. For this reason, the concept of two-state reactivity (20) (which implies transitions between two potential surfaces with different multiplicities) can prove to be essential for reactions involving transition metal ions.

An example of a reaction that cannot be described by a single potential energy surface is provided by the reaction of the Fe^+ ion with hydrogen and alkanes (18). The 4F first excited state is observed to be much more reactive than the 6D ground state, although the energy difference between these two states is only about 0.25 eV. Nevertheless, Fe^+ (6D) ions react with alkanes along pathways that must involve quartet surfaces (see *Theory (Energies and Potential Energy Surfaces): Transition Metals*).

These nonadiabatic reactions are particularly important for polyatomic systems, because the transition probability is a cumulative process. Therefore, even a weak spin-orbit coupling constant can bring about a substantial rate constant (or reactive cross-section) if the lifetime of the molecular ion is long enough (in a unimolecular dissociation reaction), or if a long-lived collision complex is formed (in a bimolecular reaction), because the nonadiabatic region is then crossed many times.

If, however, the multiplicities are the same, one has to establish a distinction between two possibilities (3) discussed below.

5.2 Case (b1): Avoided Crossings

These are characterized by adiabatic surfaces that assume locally the shape of hyperbolic cylinders (Fig. 4). This situation is encountered when the two

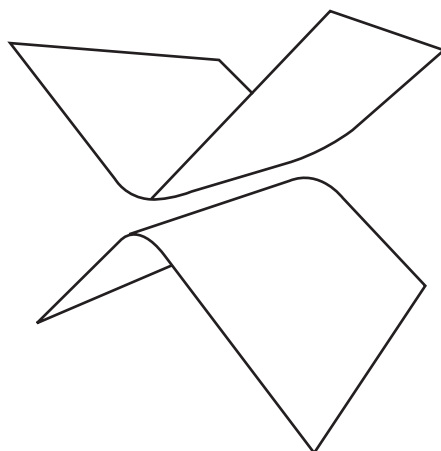


Figure 4
Avoided crossing between two adiabatic surfaces.

states have the same multiplicity and the same group-theoretical symmetry (21, 22).

5.3 Case (b2): Conical Intersections

These occur where the two adiabatic potential energy surfaces present the topology of a double cone joined at an apex (Fig. 2) (3–6). They are found when the two interacting states are characterized by the same multiplicity but with different group-theoretical symmetry species. However, it has been realized that conical intersections also occur even between two states with the same symmetry species (5, 6).

Conical intersections lead to ultrafast radiationless transitions and ultrashort decay times, i.e., the lifetime of the electronically excited state is of the same order of magnitude as a vibrational period (lifetime $\tau \approx 10^{-13}$ s) (23).

Conical intersections are occasionally involved in the fragmentation of cations (3, 23–26). The situation depicted in Fig. 2 is encountered, for example, in the dissociation of the formaldehyde cation leading to $H_2 + CO^+$. The reason is that the H_2CO^+ cation dissociates in its 2B_1 state, whereas a symmetrical extension of the two CH bonds would lead to a pair of fragments $H_2 + CO^+$ in a 2A_1 state. By distorting the reaction path, the symmetry constraints are lowered. If the molecular ion is bent out of plane, the symmetry species 2B_1 and 2A_1 both become $^2A'$. The most favorable reaction path now goes around the lower cone. By making this detour, it reaches the dissociation valley without encountering a large energy barrier. From the point of view of chemical kinetics, this more complicated reaction path offers two significant advantages over the straightforward mechanism (i.e., the symmetrical extension of the two

CH bonds): (i) the activation energy is reduced (as shown in Fig. 2); and (ii) the electronic nature of the adiabatic wave function changes gradually along the circular path (i.e., one no longer has to switch abruptly between two different electronic states). A disadvantage is that a significant curvature of the reaction path is introduced. This curvature is known to decrease the rate constant. As a matter of fact, a sharp curvature of the reaction path is thought to throttle the reactive flux very efficiently, and thus to constitute an efficient bottleneck or transition state.

6. Examples of Important Processes Involving Nonadiabatic Interaction

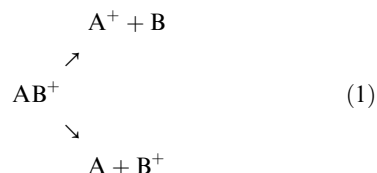
6.1 Validity of Statistical Theories

All statistical theories of mass spectra assume fast internal energy randomization within the reactant before dissociation takes place. Nonadiabatic processes here play a leading role when electronic states are initially populated. The collision between a neutral molecule and a 70 eV electron leads to a series of Franck-Condon transitions to various electronically excited states of the molecular ion. Alternatively, molecular ions may be generated by autoionization, which consists of a transfer of part of the internal energy of the ionic core (either vibrational or electronic) to a Rydberg electron which is then ionized. Autoionization is usually a very fast process that necessarily requires a breakdown of the Born-Oppenheimer approximation. Once these electronically excited states of the molecular ion are produced, they are converted to the ground state by a sequence of fast radiationless transitions. Conical intersections are mainly responsible for this conversion of electronic energy into vibrational energy, because they are at the same time very numerous and highly efficient (the lifetime for this kind of radiationless transition is, as already mentioned, of the same order of magnitude as a vibrational period) (23). Most interestingly, the vibrational energy that appears in this way is observed to be randomized over several vibrational degrees of freedom (25, 26). Thus, these fast internal conversions are a first step towards the generation of a microcanonical ensemble postulated by quasi-equilibrium theory (QET). This confirms an early hypothesis according to which fast nonradiative nonadiabatic transitions between excited electronic states of the molecular ion and its ground electronic state bring about energy randomization (see *Theory (Reactions): Statistical Theories in Mass Spectrometry*).

6.2 Charge Transfer Processes and Ion-molecule Reactions

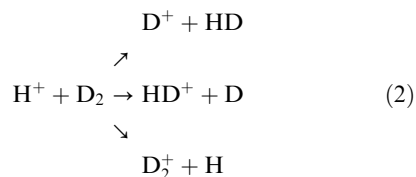
Consider a charge exchange process $A^+ + B \rightarrow A + B^+$, or a competitive decay where a pair of

fragments is generated with two possible locations of the charge, i.e.,



Reactions of this kind cannot in principle be described by a ground state potential energy surface alone. Two different electronic states are necessarily involved in such a process (27). The reason is that in a bimolecular charge transfer process the positive hole is located around a different partner at the beginning and at the end of the reaction. The two pairs of fragments $A^+ + B$ and $A + B^+$ necessarily derive from two different electronic states of the quasimolecule, i.e., one pair will correlate with the ground state AB^+ whereas the other pair correlates with an excited state $(AB^+)^*$. Therefore, a correct description of these processes necessarily involves consideration of two more or less strongly interacting potential energy surfaces. In such cases, it is problematic to look right away for a conventional transition state. Unless the splitting between the two adiabatic potentials is so large that the interaction can be neglected, the feature that controls a charge exchange reaction or either branch of the competitive process of Eqn. (1) cannot be a saddle point. It is highly advisable to check whether there exists a region where the nonadiabatic interaction is strong, i.e., an avoided crossing, or a conical intersection, or a crossing between two states with different multiplicities.

Let us introduce a few examples. One of the first examples to be thoroughly studied is offered by the simplest of all bimolecular reactions, involving three hydrogen nuclei bound by two electrons. As a consequence of an avoided crossing between the two lowest singlet potential energy surfaces of H_3^+ , the set of competitive reactions of Eqn. (2) is known to involve a nonadiabatic process (2):



This is also the case for the apparently simple resonant charge transfer process $He^+ + He \rightarrow He + He^+$ which has been shown to involve an interplay between two electronic states, one gerade and one ungerade.

The protonation of ammonia provides an additional example of a (weak) nonadiabatic interaction

(28). Because the energy of the $\text{NH}_3 + \text{H}^+$ pair is higher than that of $\text{NH}_3^+ + \text{H}$, generation of NH_4^+ in its ground state by adding a proton to ammonia must involve a jump between two adiabatic surfaces. Conversely, the dissociation of the ammonium ion should generate NH_3^+ and H if the reaction proceeds in an adiabatic way.

Charge exchange reactions are characterized by the concept of “reaction window,” which is of great diagnostic value (29–31). In these reactions the nonadiabatic region is crossed twice (once as the collision partners approach and once as they separate, see Fig. 5). Therefore, a successful charge transfer implies remaining in the original diabatic state (with a probability equal to p) and then switching to the other diabatic state (with a probability equal to $1-p$). The compound probability is thus equal to $p(1-p)$. An equally successful sequence implies these two events in the reverse order: first switching, then not switching, with an overall probability equal to $(1-p)p$. The total probability is thus the sum of the probabilities of these two sequences, i.e., $2p(1-p)$. The reaction cross-section should be equal to zero both when $p=0$ or when $p=1$, and should assume its maximum value when $p=0.5$. For a given curve, p is a function of the nuclear velocity. Hence, when plotted as a function of the velocity of the two partners (measured in the center-of-mass reference frame), the reaction cross-section is expected to assume a bell-

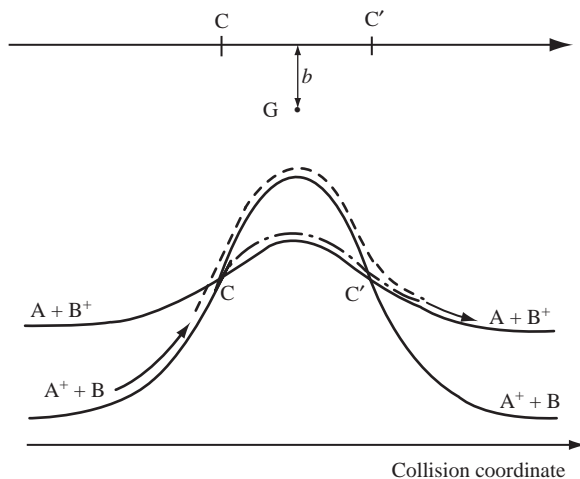


Figure 5

Top: glancing collision between a fast-moving ion and a target gas G (b is the impact parameter). Bottom: potential energy curves for an endothermic charge exchange $\text{A}^+ + \text{B} \rightarrow \text{A} + \text{B}^+$. The charge is not transferred in one step at the point of closest approach, but at points C or C' where the diabatic curves happen to cross.

shaped curve, whose width determines the so-called reaction window (see *Thermochemistry (Methods): Charge Transfer Equilibria and Complexes*).

6.3 Collisionally Activated Dissociation (CAD)

When a highly accelerated molecular ion collides with a neutral target gas, it fragments according to a pattern that is often similar to that obtained by electron impact. The mechanism of CAD is a sequential process involving several nonadiabatic interactions (32–34). In a first stage, an inelastic collision with a target gas G converts the ground state ion M^+ to one or several electronically excited states M^{+*} . In a second step, these excited ions M^{+*} are converted back to the ground state M^+ via a cascade of radiationless transitions (Fig. 6). This internal conversion considerably increases the available amount of vibrational energy and brings about fragmentation. The second step is thus entirely analogous to that observed in a usual mass spectrum generated by electron impact, thereby accounting for the similarity between the two breakdown patterns. Therefore, a CAD spectrum can often be described by statistical theories. The excitation mechanism is sometimes said to be vertical or Franck–Condon-like. Note, however, the differences with the transitions studied in electronic spectroscopy. An absorption spectrum results from a radiative transition taking place “vertically,” i.e., at the equilibrium distance of the molecule (or molecular ion) to be excited. In CAD, excitation results from a nonradiative transition between two electronic states of the supermolecule formed by the molecular ion and the target gas at either of two values of the collision coordinate (Fig. 6). The excitation process is therefore very similar to the charge exchange mechanism depicted in Fig. 5.

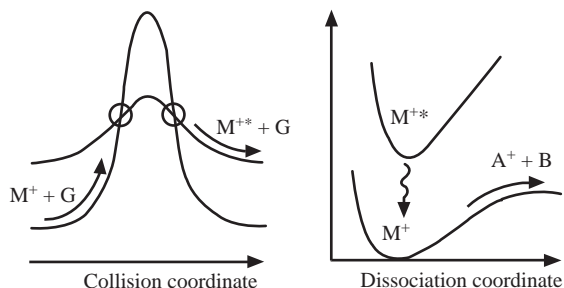


Figure 6

Sequential mechanism involved in collisionally activated dissociation. Left: inelastic collision with a target gas G leading to an electronically excited projectile ion M^{+*} . Right: internal conversion of M^{+*} followed by dissociation into $\text{A}^+ + \text{B}$ fragments.

Of course, when the collision energy is less than the keV range, CAD can occur on a single potential energy surface and need not involve nonadiabatic interactions (see *Collisional Activation and Dissociation: Methodology*).

6.4 Isolated State Dissociation

In an avoided crossing situation, two reaction channels are available. If, furthermore, the Massey parameter is not very different from unity, then the reactive flux branches into both channels, with distinct chemical outcomes.

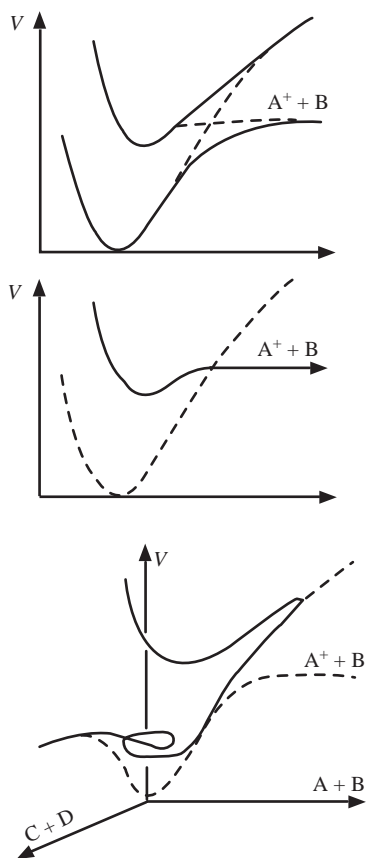


Figure 7
Coexistence of two reaction mechanisms in isolated state dissociation. Top: adiabatic (solid lines) and diabatic (dashed lines) potential energy curves of an avoided crossing. Middle: the molecular ion dissociates to $A^+ + B$ fragments via the direct diabatic path. Bottom: the alternative adiabatic path leads to internal conversion to the ground state causing energy randomization and dissociation to other fragments via a statistical mechanism.

In some cases, *ab initio* calculations have detected examples where an avoided crossing between two electronic states brings about a partitioning of the reactive flux (3, 21, 22, 24, 26). The major fraction of the nuclear trajectories is converted to the ground state potential energy surface of the molecular ion and undergoes statistical dissociation. However, a minor fraction of the nuclear trajectories generates fragments by a fast, diatomic-like nonstatistical mechanism taking place on the surface of the upper electronic state. This (rare) phenomenon, which has been termed isolated state decay, is illustrated schematically in Fig. 7. Examples of it can be found in the production of CH_3^+ ions from CH_3OH^+ (21) and of $C_2H_3^+$ fragments from $C_2H_3F^+$ (22).

7. Concluding Remarks

The description of a chemical reaction in terms of nuclei moving on a single potential energy surface is simple and appealing. However, nonadiabatic interactions occur when potential energy surfaces corresponding to different electronically excited states are close in energy in a certain range of internuclear distances. Complications of this kind are often encountered in molecular ions. The reason is that open-shell systems are characterized, already at moderate internal energies, by a much higher density of electronic states than closed-shell molecules. Therefore, many processes occurring in ionic systems that superficially appear straightforward actually require inclusion of nonadiabatic effects for their correct explanation.

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Classical Trajectory Simulations

1. Introduction

Classical trajectory simulations have been extensively used to study a broad range of chemical processes in mass spectrometry (1–5), including ion–molecule association (1–3), intramolecular and unimolecular dynamics of ion–molecule complexes (3), collision-induced dissociation (CID) (4), surface-induced dissociation (SID) (5), secondary ion mass spectrometry (SIMS) (6), and matrix-assisted laser desorption ionization (MALDI) (7). In a trajectory study, the motions of the atoms for an ensemble of molecules are simulated by solving the classical equations of motion, usually in the form of Hamilton’s equations

$$\frac{\partial H}{\partial q_i} = \frac{\partial V}{\partial q_i} = \frac{-\partial p_i}{\partial t} \quad \text{and} \quad \frac{\partial H}{\partial p_i} = \frac{\partial q_i}{\partial t} \quad (1)$$

where the sum of the kinetic $T(\mathbf{p}, \mathbf{q})$ and potential $V(\mathbf{q})$ energies of the molecule is the system’s Hamiltonian

$$E = H = T(\mathbf{p}, \mathbf{q}) + V(\mathbf{q}) \quad (2)$$

Newton’s equations may also be used to solve the classical equations, i.e.

$$-\frac{\partial V}{\partial q_i} = F_i = m_i \frac{\partial^2 q_i}{\partial t^2} \quad (3)$$

For the most general case, as for an internal coordinate representation (8), T depends on both the