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The Mechanism of Non-adiabatic Bimolecular Reactions

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The dynamics of bimolecular non-adiabatic elementary process in gases are discussed. The inelastic processes occurring in collisions between atoms and dia-atomic molecules and exchange and decomposition reactions are considered within the framework of the semiclassical description of collisions based on the instantaneous jump model of the reacting system between adiabatic potential energies surfaces.
The bibliography includes 121 references.

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1. INTRODUCTION

This review discusses the mechanisms of elementary non-adiabatic bimolecular gas-phase reactions, i.e. reactions involving a change in the electronic states of reactant molecules. These processes have been attracting increasing attention in connection with new research possibilities which have arisen as a result of applying the techniques of molecular beams and laser fluorescence which yield extremely detailed information about the initial states of the reactants and products. Non-adiabatic processes are much more common than might be supposed on the basis of the space devoted to them in recent books and reviews on elementary processes[1-3].

This paper is an attempt to fill part of the existing gap in the review literature on the mechanisms of elementary non-adiabatic reactions. The author has restricted the treatment to a discussion of the simplest (and therefore the best studied) non-adiabatic reactions—the reactions of atoms with diatomic molecules.

The review has been arranged as follows. Initially (Section 2) there is a brief discussion of the classification of non-adiabatic processes and general information about the mechanisms of non-adiabatic interaction is presented. The next section (Section 3) deals with the influence of non-adiabatic effects on the exchange of rotational and vibrational energies in processes without a redistribution of atoms. Sections 4 and 5 are devoted to non-adiabatic exchange and collisional dissociation reactions. The literature references include mainly recent studies associated directly with research on specific non-adiabatic processes. Instead of direct references to studies in the past years, recent books[1-4] in which the relevant processes are discussed and the original literature is given, are referred to.

2. DEFINITION OF NON-ADIABATIC PROCESSES

Adiabatic Potential Energy Surfaces

In the general case where an atom A collides with a diatomic molecule BC, the following elementary processes are possible:

$$A + BC \begin{cases} \rightarrow A + BC - \text{(elastic and inelastic collisions)} \\ \rightarrow AB + C \text{ (exchange)} \\ \rightarrow AC + B \text{ (exchange)} \\ \rightarrow A+B+C \text{ (dissociation).} \end{cases} \quad (1)$$

Analysis of the mechanism of any of these processes in the gas phase is based on the study of the dynamics of the elementary collision step. Such investigation yields the reaction cross-section which, together with the distribution of the reactant molecules between initial states, fully determines the rate of reaction (see Kondrat'ev and Nikitin[1], §8). The calculation of the cross-section constitutes a fairly difficult problem in classical or quantum mechanics and simplifying assumptions are always made. These simplifications concern two aspects of the problem. The first is associated with the attempt to exclude from consideration the dynamics of electron motion in the reacting system of atoms and molecules and to formulate the problem in terms of the motion of atomic nuclei alone. This is achieved by employing the adiabatic approximation[1,4], within the framework of which one introduces the concepts of the potential energy surfaces of the nuclei $U_n(R)$, which depend on the set of nuclear coordinates R and refer to a given electronic state n. Since the creation of the quantum theory of molecules, the calculation of potential energy surfaces has been one of its most important tasks (see the relevant reviews[5,6]).

Another aspect of the problem consists of the study of the dynamics of the motion of the nuclei of the reacting molecules, which is usually treated in terms of the motion of the characteristic point of the system along the specified potential energy surface from the region corresponding to the initial molecules (reactants) to that of the reaction products. This approach to the theory of elementary processes has developed strongly during the last 10–15 years and a major proportion of the important results have been obtained by computer calculations of reaction probabilities and cross-sections.

However, there is a whole class of chemical reactions which cannot, in principle, be interpreted in terms of the motion of the system along *one* fixed potential energy surface, i.e. a significant feature of the mechanism of these reactions is a change in the electronic state of the system. To investigate the dynamics of these reactions, called non-adiabatic, it is necessary to go beyond the framework of the adiabatic approximation. The theory corresponding to this generalisation can be formulated as follows. One of the formulations employs the adiabatic potential energy surfaces $U_n(R)$ as the zeroth approximation with additional allowance for the transitions between them (non-adiabatic transitions). This approximation will in fact be employed below.

Adiabatic potential energy surfaces are defined as the eigenvalues of the electronic Hamiltonian H_{el} of a system ABC with a fixed configuration of the nuclei. However, in terms of this general formulation, the problem of finding $U_n(R)$ and the corresponding adiabatic electronic functions φ_n usually cannot be solved. Any approximate solution is equivalent, in a certain sense, to the solution of the exact problem with a Hamiltonian H^0_{el} differing from H_{el}. The corresponding eigenfunctions φ^0_n and the eigenvalues $U^0_n(R)$ are associated with the so-called rough adiabatic approximation. If the difference between H_{el} and H^0_{el} is not great, then the $U^0_n(R)$ constitute a satisfactory approximation to the $U_n(R)_0$ in those regions of the configuration space of the nuclei where the difference $U^0_n(R) - U^0_{n'}(R)$ is appreciably greater than the matrix element $\delta H_{nn'}$ for the interaction ($\delta H = H_{el} - H^0_{el}$). Hence it follows that the regions of the intersections of the states of the rough adiabatic approximation, where the above condition is known not to hold, must be specially investigated since such an intersection can either also occur for adiabatic surfaces or be replaced by a close approach of the adiabatic surfaces (the so called quasi-intersection).

The general theory[7,8] and also its specific application to a three-atom system[4,9] establishes the characteristics of the intersection of the $U_n(R)$ and $U^0_n(R)$ states.

Depending on the effects which it is desirable to include in the study of the reaction dynamics, the Hamiltonian H^0_{el} is chosen with different degrees of approximation and the possibility of neglecting certain terms in H_{el} when specifying H^0_{el} is determined by the condition that these terms have little influence both on the structure of the adiabatic surfaces and on the probability of non-adiabatic transitions. In this connection we may mention the following approximations.

a. Neglect of magnetic interactions (spin–orbit and spin–spin). The energy of such an interaction varies from several hundredths of an electron-volt to 1 eV for heavy atoms (for example the iodine atom). In this approximation the overall electron spin is conserved so that any processes described by relation (1) should follow the Wigner rule: among the possible spin states of the products, there should be a state identical with one of the spin states of the initial reactants. Magnetic interactions can be neglected in constructing the potential energy surfaces for a system of light atoms. However, they must almost always be taken into consideration (systems comprising H and He atoms are an exception) in calculations of the probabilities of non-adiabatic transitions.

b. Neglect of electron correlation effects. Within the framework of this approach, based on the one-electron approximation, it is possible to formulate a number of simple rules for the qualitative construction of surfaces (for example the Woodward–Hoffmann principle of the conservation of orbital symmetry[11–13] or the employment of correlation diagrams for molecular orbitals[14]). Since the electron correlation energy is of the same order of magnitude as the energy of the splitting of the atomic states which arise from a single configuration (1–2 eV), the one-electron approximation is not applicable in a quantitative calculation of the surfaces. Nor can it be used to calculate the probability of non-adiabatic transitions.

c. Neglect of the change in electron correlation on mutual approach of the initial reactants. In constructing H^0_{el} within the framework of this approach account is taken first of the electron correlation in isolated atoms and molecules and the interaction between the colliding species is taken into account only in the following stage. This method, which is a generalisation of the Heitler–London method to include many-electron systems, yields the correct type of adiabatic states for large intermolecular distances[15]. We may note that the employment of this approximation for smaller distances leads to a qualitative proof of the familiar Polanyi–Semenov correlation[1] between activation energies and heats of reaction in a series of similar reactions.

Although for a fairly small perturbation δH the U_n^0 and U_n surfaces proved to be close in most of the configuration space of the nuclei, the corresponding states are specified by *different* sets of electronic quantum numbers. Therefore the classification of processes as adiabatic or non-adiabatic within the framework of any rough adiabatic approximation can frequently change when the approximation is refined. The consequent ambiguity in the definition of non-adiabatic reactions must be always borne in mind. However, the final result of the study of the dynamics—the calculation of the reaction probabilities or cross-sections—is independent of the ambiguity of the definition, provided that non-adiabatic transitions have been taken into account correctly in the solution of the problem.

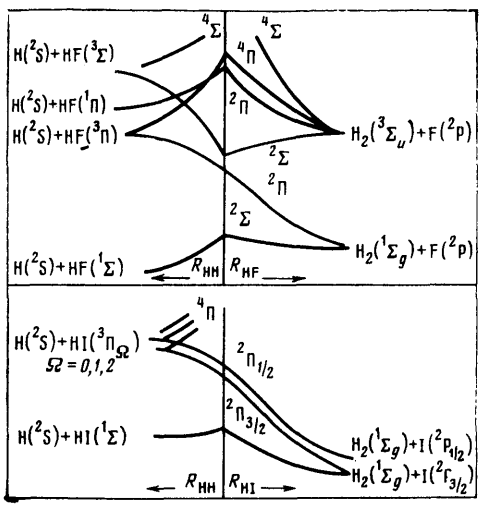


Figure 1. Correlation diagrams for the electronic terms of the reaction H + HF → H_2 + F (weak spin—orbital interaction, upper Figure) and H + HI → H_2 + I (strong spin—orbital interaction, lower figure) with a linear configuration of the nuclei.

Numerous examples of the correlation of the electronic states of a three-atom system are quoted in a review[16]. Here we shall mention only one example illustrating the influence of the spin-orbital interaction on the structure of the surfaces for an HHX system (X is a halogen atom). Fig. 1 presents the cross-sections of the surfaces of the linear HHF system which have been calculated by the semiempirical method of diatomic complexes in molecules[17]. The left-hand side of the Figure corresponds to the pathway $\infty > R_{HH} \geq R^{\circ}_{HH}$, $R_{HF} = R^{\circ}_{HF}$ and the right hand side corresponds to the pathway $R_{HH} = R^{\circ}_{HH}$, $R^{\circ}_{HF} \leq R_{HF} < \infty$. When the linear configuration of the nuclei breaks down, the $^2\Sigma$ and $^4\Sigma$ states (in the calculation of which the spin-orbital interaction is neglected, as in the case of the Π states, because it is small for the F atom) are classified as the $^2A'$ and $^4A'$ states in the C_S symmetry group, the corresponding energies being somewhat altered.

The $^2\Pi$ and $^4\Pi$ states are split as well as displaced and are classified as $^2A'$, $^2A''$, and $^4A'$, $^4A''$.

On passing from F to heavier halogens, account must be taken of the spin-orbit interaction in plotting the diagrams. The lower part of Fig. 1 illustrates qualitatively these changes in the disposition of the states for the HHI system which arise under these conditions. For example, the degeneracy of the state $^2\Pi$ is lifted; instead there arise two components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, which are correlated with different states of the I atom. When the linear configuration is distorted, the states are not split further: they remain doubly degenerate with respect to the spin projections as a consequence of Kramers theorem[7].

Description of Non-adiabatic Transitions

Non-adiabatic transitions between potential energy surfaces are due to the dynamic interaction of electrons and nuclei. A consistent quantum theory formulates the problem of describing the transitions in terms of a system of coupled wave equations. In this formulation the problem can be solved (and has been solved successfully) for collisions of two atoms when the potential energy surfaces simplify into potential energy curves (a system of equations in a single variable R). The minimum dimensionality of the equations whose solution is significant in connection with the study of the dynamics of non-adiabatic reactions is two (linear collision of an atom with a diatomic molecule). However, this problem cannot be solved at present even on the best computers: the quantum solution has been obtained so far only for the two-dimensional adiabatic problem of the reaction of a hydrogen atom and an H_2 molecule. This factor and also the fact that even the solution of a real multidimensional adiabatic problem can be obtained only within the framework of the classical description necessitates the employment of semiclassical methods for calculating the probabilities of non-adiabatic transitions, the essential features of which are as follows.

The study of the problem of non-adiabatic transitions shows that the dynamic interaction is most vigorous in the region corresponding to the approach or intersection of the states. The main parameter determining the extent of the interaction is the ratio of the frequency of the oscillation of electrons between the levels, $\omega(R) = |U_n - U_n'|/\hbar$, to the "frequency" $1/\tau$ characterising the rate at which the nuclei traverse the region of interaction. If the parameter $\xi = \omega\tau$ is large, it is possible to neglect the non-adiabatic transitions[4,18,19]. Non-adiabatic transitions must be taken into account only in the regions of the configuration space of the nuclei where $\xi \leq 1$ or ξ becomes zero. The extent l of this region is then important. If the extent is small, i.e. l is appreciably smaller than the characteristic dimensions L which define the region of interaction of the three-atom system, then the semiclassical approximation suggests the following method for describing non-adiabatic transitions which makes maximum use of the simplicity of the classical description of the motion of the representative point in adiabatic regions. The representative point moves along the potential energy surface corresponding to the initial electronic states of the initial reactants until the attainment of the region of strong non-adiabatic coupling. In this region the system executes a jump from the initial surface to a neighbouring surface with a probability P_1, which depends on the parameters of the surfaces in this region; the probability that the system remains on the initial surface is $1 - P_1$. Subsequently the motion is

continued on two surfaces—the first and second surfaces—the probabilities $1 - P_1$ and P_1 being associated with the corresponding trajectories. The motion continues until each trajectory again reaches the non-adiabatic regions. In these regions each trajectory "branches" once more. The consecutive repetition of the steps involving the adiabatic motion on the surfaces and the corresponding jumps yields the semiclassical picture of the process. Clearly the trajectories characterised by different "histories" of the jumps between the potential surfaces and having different probabilities P_k contribute to the set of final states (for example to the energy range $\hbar\omega$ near the vibrational energy E_{vibr} of the molecule formed), which is identified in the semiclassical approximation with the population of the quantum level. Then the overall probability of the process is defined by the sum of the probabilities P_k.

Two general objections may be raised against the semiclassical method: (a) failure to include quantum effects in the adiabatic motion of the system on the surface, (b) inaccurate definition of the concept of the trajectory in the non-adiabatic region where the jump takes place, and (c) failure to consider interference effects in adding the probabilities (and not the probability amplitudes) in the final state. All these objections also apply to the semiclassical description of atomic collisions, the limits of applicability of which are well known. The information accumulated so far concerning the accuracy of the semiclassical method and ways for improving it[22] suggests that the semiclassical approach is the most promising in the study of the dynamics of non-adiabatic processes.

For a specific calculation of the overall probability of a non-adiabatic process, it is necessary to know the probabilities P_k of the individual transitions. The calculation of these quantities reduces to the solution of the system of equations for non-adiabatic coupling, which can be incorporated in a single computer program. However, it is possible to simplify the dynamic calculation significantly using in the transition probabilities calculated independently within the framework of specific models. A number of such models are known at present[18]. The simplest of these is the Landau—Zener model[1,4,19], which can be used to calculate P provided that the cross-sections of the adiabatic surfaces along the part of the projectory $\mathbf{R} = \mathbf{R}(t)$ in the region of the interaction can be fairly satisfactorily approximated by two coupled hyperbolae. States of this kind are known to arise naturally[1,4] when the surfaces U_1 and U_2 are obtained by diagonalisation of the second-order matrix in a basis set of the intersecting states of the rough adiabatic approximation. Then the expression for the probability of non-adiabatic transition is

$$P = \exp[-2\pi a^2/\hbar\,|F_{1R} - F_{2R}|\,v_R] \quad , \qquad (2)$$

where $2a$ is the minimum distance between the states U_1 and U_2, F_{1R} and F_{2R} are the slopes of the lines asymptotic to the hyperbolae along the section of the trajectory $\mathbf{R}$, and v_R is the rate of motion of the system in the region of the transition. It is seen from Eqn. (2), that, for low values of the parameter $2\pi a^2/\hbar\,|F_{1R} - F_{2R}|\,v_R$, the system executes transitions between the adiabatic states with a high degree of probability. Hence follows the usefulness of the concept of diabatic states or diabatic surfaces, defined as surfaces which are followed by the system with a high probability when the velocity is sufficiently high. Evidently the probability P' of the transition between the diabatic states is expressed in terms of P by the relation $P' = 1 - P$, so that we obtain for the Landau–Zener model

$$P' = 1 - \exp[-2\pi a^2/\hbar\,|F_{1R} - F_{2R}|\,v_R] \quad . \qquad (3)$$

For high velocities, the probability of the transition between the diabatic states is low and is given approximately by

$$P' = 2\pi a^2/\hbar\,|F_{1R} - F_{2R}|\,v_R \quad . \qquad (4)$$

In practical calculations upper and lower limits are imposed on the parameter $2\pi a^2/\hbar\,|F_{1R} - R_{2R}|\,v_R$, since unduly low probabilities of the transition (and hence of branching) between adiabatic or diabatic surfaces usually need not be taken into consideration. Bearing in mind these limitations and using the available estimates of the extent of the transition regions l,[18] it is possible to show that the condition $l \ll L$, for which the description of the transitions in terms of jumps is satisfactory, holds when the energies are less than 10 eV.

3. EFFECT OF NON-ADIABATIC CONDITIONS ON THE EXCHANGE OF ROTATIONAL AND VIBRATIONAL ENERGY

Energy exchange processes in the collisions between an atom A and a diatomic molecule BC are usually considered in terms of the trajectory on the potential energy surface, which for $R_{A\text{-}BC} \to \infty$ correlates with the electronic state of the uncoupled system A + BC. If the electronic states of A and BC are non-degenerate, such a correlation defines a single potential energy surface, which is used subsequently in the dynamic calculation. On the other hand, even if only one of the two species has a degenerate electronic state, the interaction between A and BC lifts the degeneracy. Thus several closely spaced potential energy surfaces arise and in the limit $R_{A\text{-}BC} \to \infty$ these are correlated with the degenerate electronic state of the uncoupled system A + BC. If is found that the existence of several close surfaces alters significantly the probabilities of the rotational and vibrational transitions compared with the simplest case of a single surface, where it is possible to employ the adiabatic approximation.

Rotational Transitions

Recent experiments on rotational transitions in the $Na_2^*(^1\Pi)$ [21,22] and $Li_2^*(^1\Pi)$ [23,24] molecules, induced by collisions with inert gas atoms, showed that, together with the $j' - j = \Delta j = \pm 2$ transitions (the usual selection rules for rotational transitions in diatomic molecules with identical nuclei), there is a high probability of transitions with $\Delta j = \pm 1$, and the cross-sections of the one-quantum transitions depend strongly on the sign of Δj. A quantum interpretation of this effect has been given[25,26]. Here we shall consider the simpler semiclassical interpretation based on symmetry considerations alone.

One of the integrals of motion of the moving atom + diatomic molecule system is the overall angular momentum J. In the semiclassical approximation the vector J is identified with the vector of the relative angular momentum l, which is valid subject to the condition $l \gg j$, where j is the angular momentum of the molecule. In this approximation the trajectory of the relative motion of A and BC must be regarded as planar and a reflection in this plane is an operation which commutes with a non-stationary Hamiltonian.

If the electronic state of the molecule BC is defined in such a way that it has a certain symmetry ϵ ($\epsilon = 0, 1$) with respect to reflection in the plane passing through the molecular axis [i.e. the electronic wavefunction acquires the multiplier $(-1)^{\epsilon}$ on reflection in this plane], then the overall wave function (the electronic-rotational function) acquires the multiplier $(-1)^{j-m+\epsilon}$ on reflection in the collision plane[7]. Since the reflection in this plane is an exact symmetry operation, the collision can give rise to transitions between states with the same symmetry relative to the collision plane. Therefore the initial quantum numbers j, m, and ϵ and the final numbers j', m', and ϵ' are linked by the relation $j - m + \epsilon = j' - m' + \epsilon' + 2p$, where m denotes a projection of j onto the axis perpendicular to the collision plane and $2p$ is an even number.

If the electronic state of the molecule is non-degenerate, then ϵ is defined unambiguously and $\epsilon = \epsilon'$. This condition does not alone impose any limitations on the variation of j and therefore for low anisotropy of the interaction the most probable transitions correspond to the minimum change in j, i.e. $\Delta j = \pm 1$. If the molecule BC contains identical atoms (B = C), then the interaction potential of A and B_2 has an additional symmetry, which forbids transitions involving a change in j by an odd number. It follows from this selection rule with respect to m and from the relations quoted above that j can change only by an even number. Therefore the minimum permissible change in j for diatomic molecules with identical nuclei in a non-degenerate electronic state is ± 2.

If the molecule BC is in a degenerate electronic state, then there are always two components of the electronic eigenfunction with different ϵ. Therefore, even for molecules with identical nuclei, transitions with $\Delta j = \pm 1$ are allowed, provided that ϵ changes simultaneously: under these conditions, the symmetry of the overall wavefunction remains unchanged in the transition.

Thus the degeneracy of the electronic state leads to a major effect in the rotational relaxation of diatomic molecules with identical nuclei—the appearance of transitions with $\Delta j = \pm 1$ as well as transitions with $\Delta j = \pm 2$.

Vibrational Transitions

An experimental study of the vibrational relaxation of diatomic molecules revealed a number of instances of "anomalously" rapid deactivation of vibrations in collisions. In this case the standard defining the "normal" rate of deactivation is the average probability $\langle P_{10} \rangle$ of the transition (the $v = 1 \rightarrow v = 0$ transition) for diatomic molecules with identical nuclei or for molecules with a low asymmetry in a single gas-kinetic collision with the molecules of the heat reservoir which are all of the same type. The theory of the vibrational–translational energy exchange ($T - V$ processes) (see, for example, Refs. 1, 3, and 4) predicts the following approximate relation between $\langle P_{10} \rangle$ and the temperature T of the heat reservoir, the frequency ω of the vibrations of the molecule being deactivated, the reduced mass μ of the colliding molecules, and the radius $1/\alpha$ of the action of the intermolecular potential:

$$\ln \langle P_{10} \rangle = -\frac{3}{2}(4\pi^2\omega^2\mu/\alpha^2 kT)^{1/3} + A , \qquad (5)$$

where A is a function of the above parameters, which shows a smaller dependence on them than the first term on the right-hand side of Eqn. (5). This relation constitutes the basis for the widely used semiempirical correlation of the $\langle P_{10} \rangle$ for different molecules over a wide temperature range[1]. Naturally, under these conditions a high accuracy is not achieved, but even approximate validity of Eqn. (5) is sufficient for subsequent discussion.

An illustration of "normal" VT processes may be provided by the following reactions which have been fairly fully investigated over a wide temperature range:

$$\begin{aligned} &N_2(v=1) + N_2(v=0) \rightarrow N_2(v=0) + N_2(v=0) , \\ &O_2(v=1) + O_2(v=0) \rightarrow O_2(v=0) + O_2(v=0) , \\ &CO(v=1) + CO(v=0) \rightarrow CO(v=0) + CO(v=0) . \end{aligned} \qquad (6)$$

The $\langle P_{10} \rangle$ for all these processes, summarised in Fig. 42 in Kondrat'ev and Nikitin's book[1], fall within the shaded band in Fig. 2, whose width makes it possible to estimate the accuracy of Eqn. (5). In this figure $-\lg \langle P_{10} \rangle$ is plotted as a function of the dimensionless parameter $(\omega^2\mu a_0^2/kT)^{1/3}$, where a_0 is the Bohr radius. According to Eqn. (5), the slope of the band should be $(\lg e)\frac{3}{2}(4\pi^2)^{1/3} \cdot (a_0\alpha)^{-2/3}$. Comparison of this quantity with the average slope shown in Fig. 2 yields $\alpha \simeq 3.2/a_0$, which is the usual value adopted in the theory of the vibrational relaxation of diatomic molecules.

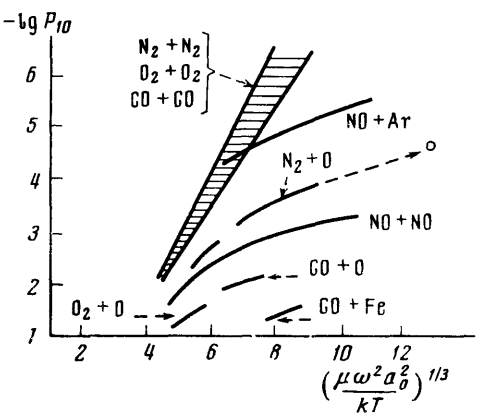


Figure 2. Probabilities of vibrational deactivation in "normal" and "anomalous" processes.

The experimental points for "anomalous" processes lie appreciably below this band. A number of anomalies have been explained by the contribution of VR processes, i.e. the transformation of the vibrational energy of the molecule into rotational energy (see Nikitin[4], §9). However, this explanation, which retains Eqn. (5) but alters the sense of the reduced mass μ, can be adduced only for processes where the reduced mass of the colliding species is much greater than the reduced mass of the molecule being deactivated. Finally, rapid relaxation can be caused by an exchange reaction if the latter is characterised by a low activation energy.

The processes with anomalously rapid relaxation known at present for which the VR mechanism is not effective are listed below (the references to the relevant experimental studies are indicated in square brackets):

$$\begin{aligned} &NO(v=1) + Ar \rightarrow NO(v=0) + Ar , && [27] \\ &NO(v=1) + NO \rightarrow NO(v=0) + NO , && [28, 29] \\ &CO(v=1) + Fe \rightarrow CO(v=0) + Fe , && [30] \\ &N_2(v=1) + O \rightarrow N_2(v=0) + O , && [31, 32, 33] \\ &O_2(v=1) + O \rightarrow O_2(v=0) + O , && [34] \\ &CO(v=1) + O \rightarrow CO(v=0) + O . && [33, 35] \end{aligned} \qquad (7)$$

The experimental $\langle P_{10} \rangle$, taken from the above investigations, are also illustrated in Fig. 2. Evidently the $\langle P_{10} \rangle$ for reactions (7) are much higher than the corresponding values for reaction (6). Thus the usual *VT* exchange model must be abandoned for reactions (7).

The only significant difference between reactions (6) and (7) is that in the first group both species involved are in a non-degenerate electronic state and in the second group one of the species has a degenerate electronic ground state. Accordingly, purely vibrational transitions are possible for the first group, while for the second group there is a possibility of both purely vibrational transitions and electronic-vibrational transitions in which the change in the vibrational state is accompanied by a transition from one adiabatic surface to another. The difference between the mechanisms of the purely vibrational and electronic-vibrational transitions can be understood most simply in terms of the model of an oscillator (molecule BC) excited by an external force (time dependent interaction between A and BC). The external force $F(t)$ acting on the oscillator consists of two components. The first component $F_a(t)$, which is comparatively large and varies with the characteristic collision time τ_c, is due to the relative adiabatic motion of A and BC. The second component $F_n(t)$, which is small and oscillates at the frequency of the splitting of the adiabatic states, arises from non-adiabatic transitions associated with the relative motion of the species. The effectiveness of these two components in exciting the oscillator is determined not only by their magnitude but also by their spectral composition, since only the Fourier component with the frequency ω excites (or deactivates) the oscillator.

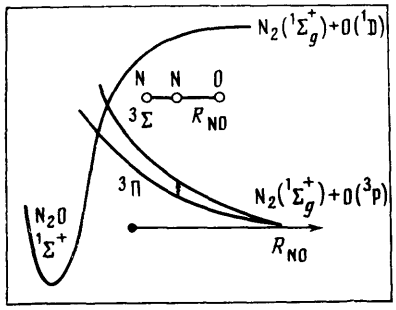


Figure 3. Electronic states of the N_2O system for a linear approach of N_2 and O.

The Fourier spectrum $f_a(\omega)$ of the component $F_a(t)$ may be bell-shaped with a characteristic width $\Delta\omega_c \simeq 1/\tau_c = \alpha u$ (u is the relative velocity of the molecules) and for $\omega \gg \alpha u$ the function $f_a(\omega)$ decreases exponentially:

$$f_a(\omega) = \int_0^\infty F_a(t)\cos\omega t\,dt \sim \exp[-\pi\omega/\alpha u] \text{ when } \frac{\omega}{\alpha u} \gg 1 \qquad (8)$$

The characteristic width of the Fourier spectrum of the component $F_n(t)$ is not determined by the condition that the frequency be equal to the reciprocal of the collision time (as for F_a) but by the maximum frequency ω_m corresponding to the transitions between the adiabatic states when A and BC move along a specific trajectory.

If the uncoupled A + BC system is in a non-degenerate state, then $F(t)$ has only one component $F_a(t)$. Under these conditions, the transition probability P_{10}, proportional to $|f_a(\omega)|^2$, varies approximately exponentially with the velocity subject to the condition $\omega/\alpha u \gg 1$. Such variation of P_{10} with the velocity in fact leads to the temperature variation of $\langle P_{10} \rangle$ in Eqn. (5), which is obtained after averaging P_{10} with respect to the relative velocities according to the Maxwell distribution. Then the parameter $(\mu\omega^2 a_0^2/kT)^{1/3}$, against which $\lg \langle P_{10} \rangle$ is plotted in Fig. 2, is equal to $(2\pi)^{-1/3}\omega a_0/u^*$, where u^* is the relative velocity of A and BC making the maximum contribution to the average transition probability.

If the uncoupled state A + BC is degenerate, it is necessary to take into account the contributions of $F_a(t)$ and $F_n(t)$. It is found[4] that, for fairly large values of $\omega\alpha/u^*$, the contribution of the force $F_a(t)$, which has a large absolute magnitude, is smaller than the contribution of $F_n(t)$, i.e. at fairly low temperatures the vibronic transitions prevail over the purely vibrational transitions. With increase of temperature (and hence with decrease of the parameter $\omega a_0/u^*$), the two contributions begin to compete and ultimately the purely vibrational transitions become more effective. Thus the theory explains the temperature variation of the "anomalous probabilities", which at high temperatures go outside the limit for the normal relation of the type of Eqn. (5).

Details of specific calculations of P_{10} for reaction (7) are quoted in the literature: NO + Ar,[37] NO + NO (Nikitin[4], §21), CO—Fe,[38] N_2 + O and O_2 + O,[39] and are discussed by Nikitin and Umanskii[40]. Here we shall mention only the following feature of the last two processes, in which there is a possibility of the formation of the intermediate complexes N_2O and O_3.

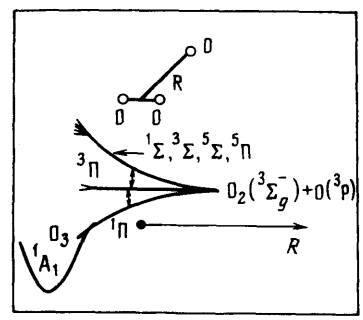


Figure 4. Electronic states of the O_3 system for a non-linear approach of O_2 and O.

The form of the states for the N_2O system (Fig. 3) shows that the vibronic transitions occur in the region where the vibration frequency is equal to the splitting of the electronic states (this region is designated by an arrow in Fig. 3), that is for energies appreciably lower than that of the intersection of the triplet states with the singlet ground state of NO_2. This rules out the possibility of forming a complex with an appreciable contribution of non-adiabatic effects in the region of the intersection of the state $^1\Sigma$ with the states $^3\Sigma$ and $^3\Pi$. This therefore throws doubt on the non-adiabatic relaxation mechanism proposed by Fisher and Bauer[41].

The form of the states for the system $O_2 + O$ (Fig. 4) shows that there is a state correlated adiabatically with the ^1A state of ozone. Therefore, in addition to adiabatic and non-adiabatic vibrational transitions involving the surfaces corresponding to the repulsion of O_2 and O, it is necessary to consider the energy redistribution as a result of the formation of the O_3 complex. Examination of the competition between various channels[39,40] based on different results[39,40] of numerical calculations on the dynamics of the O_3 system on the lower potential energy surface[42] shows that even at low temperatures the non-adiabatic and adiabatic mechanisms [but not described by Eqn. (5)] make comparable contributions.

In the CO + O system there is probably a situation intermediate between $N_2 + O$ and $O_2 + O$: the initial CO + O electronic state differs in spin from the CO_2 ground state (analogy with N_2O), but the CO + O interaction does not correspond to repulsion but to weak attraction (analogy with O_3). Clearly the theory of the relaxation of CO to O must take into account all the characteristics of this system, shown in the CO_2 decomposition reactions and in the recombination of CO and O (see, for example, Kondrat'ev and Nikitin[1] and Troe and Wagner[43]) as well as in isotope exchange reactions[44].

4. NON-ADIABATIC EXCHANGE REACTIONS

When the reacting molecules have a specified energy, he exchange reaction can usually be classified as one of he main types: the direct reaction (ricochet or explosive) or a reaction proceeding via a complex[1]. As a rule, the time of reaction is correlated with the general properties of the potential energy surface on which the reaction takes place. Since the involvement of several potential energy surfaces, frequently of completely different types, is characteristic of non-adiabatic reactions, the angular and energy distribution of the products can correspond to the existence of several reaction types. This was demonstrated for the first time in the reaction

$$Ba + Cl_2 \rightarrow BaCl + Cl\ , \qquad (9)$$

investigated spectroscopically[45,46] and by the method of molecular beams[47]. The product distribution was interpreted by postulating two potential energy surfaces correlated with the ground and excited states of the BaCl molecule.

The reactions proceeding via the formation of a long-lived complex can be described within the framework of a statistical approximation (see Kondrat'ev and Nikitin[1], Nikitin[4], and Nikitin and Umanskii's review[48]). In the simplest version of this approximation it is assumed that the distribution of the products between different electronic states, transitions between which are not forbidden by general conservation laws, is determined by a random redistribution law. However, this hypothesis is probably not valid. Calculation of the potential energy surfaces for the simplest reactions proceeding via a complex, such as

$$M + XM' \rightarrow MX + M' \qquad (10)$$

and

$$M + M'M'' \rightarrow MM' + M'', \qquad (11)$$

indicates a possible contribution of non-adiabatic effects (M, M', and M'' are alkali metal atoms and X is a halogen atom). In the first case[49] the surface leading to the excited state approaches very closely (to within 2—5 kcal mole^{-1}) the surface leading to the ground state and in the second case intersections actually occur. However, the relative contribution of the transition regions is very small, so that one cannot expect a statistical population of different electronic states. Similar processes can probably be described within the framework of a theory combining a statistical approach to the energy redistribution between different degrees of freedom for the motion of nuclei with a dynamic approach to the description of non-adiabatic transitions. Hitherto such a theory has not been developed. In this connection a purely dynamic approach is described below, in which reactions proceeding with and without a change in total spin are considered.

Reactions without a Change in Total Spin

The simplest reactions in which non-adiabatic effects are significant and which proceed in accordance with the Wigner rule are those between the inert gas atoms A^+ (A = He, Ne, Ar, Kr, or Xe) and hydrogen molecules. In these processes there may be competition between the exchange reaction

$$A^+ + H_2 \rightarrow AH^+ + H \qquad (12)$$

and the charge-transfer reaction

$$A^+ + H_2 \rightarrow H_2^+ + A\ . \qquad (13)$$

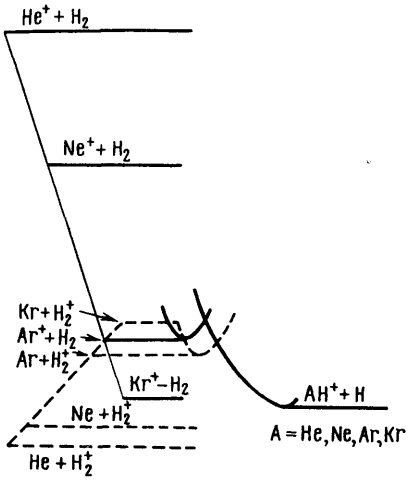


Figure 5. Correlation diagram for the electronic terms of the reactions $A^+ + H_2 \rightarrow A + H_2^+$ and $A^+ + H_2 \rightarrow AH^+ + H$.

The energy levels of the products and reactants are given in Fig. 5, where the energy minimum of the $AH^+ + H$ system (the continuous lines on the left refer to the $A^+ + H_2$ systems and the dashed lines to the $A + H_2^+$ systems) was chosen as the common zero for all the reactions. The correlation between the states on moving from left to right corresponds to motion along the reaction coordinate (12); the reaction pathway profiles then correspond to the rough adiabatic approximation. The parabolic rises on the left-hand side of the diagram correspond to the increase of energy on extension of the H—H bond (the rises for the $Ar^+ + H_2$ and $Ar + H_2^+$ systems are shown).

The potential energy surfaces for the system with A = He have the simplest structure because in this case the initial states are not degenerate and reactions (12) and (13) differ markedly in their energetics. Non-empirical[51,52] and semiempirical[53] calculations of the lowest surface yield a profile for the reaction pathway

$$He + H_2^+ \rightarrow HeH^+ + H, \qquad (14)$$

characterised by a shallow potential well (about 5 kcal mole^{-1}) and a rise equal to the endothermic heat of reaction. The calculations do not yield any indications concerning possible non-adiabatic effects. Experimental studies of reaction (14) in beams have shown[54,55] that the rise is overcome by the kinetic energy for low impact parameters and by the H_2^+ vibrational energy for high impact parameters. The theoretical study of the dynamics has been largely limited to a statistical approximation (see Nikitin and Umanskii's review[48]).

In his discussion of the cause of the low efficiency of the exothermic reaction (12) compared with the highly effective endothermic reaction (13) for A = He, Mahan[14] adduced general arguments showing that reaction (12) is non-adiabatic and that the potential surfaces which correlate with the initial states of the reactants and products, never approach one another. The same arguments remain in force also for A = Ne.[56]

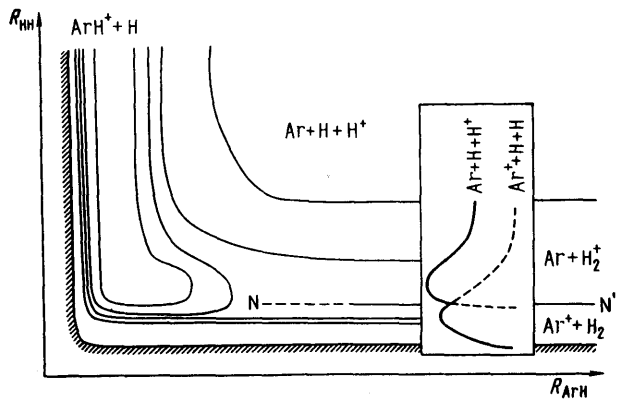


Figure 6. Schematic illustration of the potential energy surface for the collinear system ArH_2^+.

The situation changes significantly on passing to Ar and Kr. In this case the potential energy surfaces for reactions (12) and (13) are close, so that the Ar + H_2^+ and Ar^+ + H_2 diabatic states intersect when R_{HH} is varied and in the limit $R_{Ar-H} \rightarrow \infty$ the intersection is converted into a quasi-intersection for finite R_{Ar-H}. This is shown schematically in Fig. 6, where the lower adiabatic surface for the Ar—H—H linear system is illustrated. The insert illustrates the cross-sections of the surfaces of the ground and first excited states along the H—H coordinate. In adiabatic motion along this coordinate following the lowest surface the system reaches the Ar + H + H$^+$ plateau and for small H—H distances the profile of the cross-section yields the potential curve for the H_2 ground state in the repulsive region. In fact, for large R_{ArH}, the trajectory follows diabatic surfaces. In Fig. 6 this is reflected by the fact that, on approaching and intersecting the N—N′ line (which indicates the region of strong non-adiabatic interaction), the trajectory disappears from the figure or appears on it, depending on whether it approaches this line via the ground or excited state.

With decrease of R_{ArH}, the diabatic motion is increasingly replaced by adiabatic motion: in the region where the N—N′ line is shown dashed the trajectory continues to follow the lowest surface with an appreciable probability $1 - P_{12}$ also after passing through the region of non-adiabatic coupling. Finally, in the region of strong interaction, where the descent begins, the splitting between the states is high, P_{12} is close to zero, and the trajectory follows the lowest energy surface with a very high probability. Thus the dynamics is fully defined if the probability P_{12} of the non-adiabatic transition on the N—N′ line is specified. This treatment, proposed in a qualitative form by Gislason for the reactions discussed[58], was recently used as the basis for a more exact investigation of the dynamics by Chapman and Preston, who obtained a very good agreement with experiment for the cross-sections of reactions (12) and (13) (quoted by Tully[59]). When the energy is 3.36 eV, the charge-transfer cross-section appreciably exceeds the exchange cross-section (17.8 and 3.8 Å^2 respectively). However, Fig. 6 shows that the trajectories reflected from the region of turning of the dip, i.e. not leading to a reaction, result in charge transfer. Therefore dynamic calculations[60], carried out for a model adiabatic surface without taking into account non-adiabatic transitions and also the kinematic abstraction model[61] can be compared with the experimental results for the angular and energy distribution of the products.

A more complex situation arises in a reaction of the type

$$D^+ + DH \rightarrow H^+ + D_2 \qquad (15)$$

and in similar reactions for other hydrogen isotopes. Polanyi and coworkers[62] investigated the dynamics of this reaction on a non-empirical adiabatic surface. It was found, in agreement with the simplest ideas postulating the mechanism of a reaction proceeding via a stable intermediate complex, that the angular and energy distribution of the products agrees qualitatively with the predictions of the statistical theory. However, subsequent experiments[63] did not confirm the expected symmetry in the distribution of products with respect to forward and back scattering. A more detailed investigation of the structure of the surfaces showed that the surface employed in Polanyi's calculations[62] is in fact diabatic far from the potential well. It is necessary therefore to take into account the two lowest surfaces, as was done recently within the framework of semiempirical[64] and non-empirical[65] approximations. The adiabatic surface for the ground state of the H_3^+ linear system is illustrated qualitatively in Fig. 7, where the inserts show the cross-sections of the lowest (continuous line) and the first excited (dashed line) surfaces in directions perpendicular to the reaction coordinate. A surface of this type was used in recent calculations of the total and differential cross-sections of all the reactions pathways[59,66,67]:

$$D^+ + DH \begin{cases} \rightarrow H^+ + D_2 \text{ (channel } a \rightarrow b) \\ \rightarrow D + DH^+ \text{ (channel } a \rightarrow a^*) \\ \rightarrow H + D_2^+ \text{ (channel } a \rightarrow b^*) \end{cases} \qquad (16)$$

A satisfactory agreement was achieved with all the available experimental results for the differential cross-sections and the energy variation of the total cross-sections[59]. The calculated variation of the cross-sections

with the relative energy E_{transl} and for the zero-point DH level is shown in Fig. 8. This relation is simply correlated with the structure of the surfaces. The decrease of the cross-section $\sigma_{a\rightarrow b}$ of the adiabatic exchange reaction with increase of E_{transl} can be explained, by analogy with the usual adiabatic reactions, by an increase in reflection in the region of the turning of the trajectory. This effect is also shown by an increase of the charge-transfer cross-section $\sigma_{a\rightarrow b^*}$. Finally, the increase of $\sigma_{a\rightarrow b^*}$ for the non-adiabatic exchange reaction is due to the increase in non-adiabatic effects with increase of E_{transl}. If E_{transl} is sufficiently small, then the $a \rightarrow b^*$ pathway is unattainable according to the classical treatment. In this case the usual semiclassical description of the non-adiabatic transition is inapplicable and one must go outside the limits of this approximation in order to calculate the probability of the $a \rightarrow b^*$ reaction. One of the methods for extending the theory employs complex trajectories which can reach the non-adiabatic region at complex times. The probabilities of the $D^+ + DH \rightarrow H + D_2^+$ reaction were calculated in this way for low energies[68].

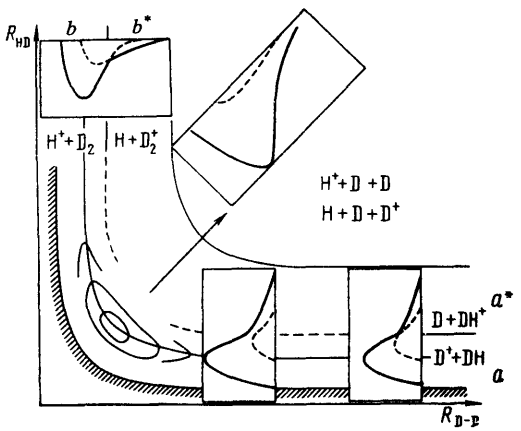


Figure 7. Schematic illustration of the potential energy surface for the collinear system HD_2^+.

Analysis of the dynamics of these reactions revealed the following important factor. Since the calculation of even the most detailed characteristic of the reaction (the differential cross-section) involves averaging with respect to at least two collision parameters (the initial phase of the vibrations and the azimuthal angle), the final result is comparatively insensitive to the transition probabilities along the lines of the quasi-intersection of the adiabatic surfaces. Therefore even comparatively rough estimates of the transition probabilities, carried out subject to the condition that the regions of the non-adiabatic transitions are unattainable on classical grounds, can yield satisfactory accuracy in the calculation of the cross-sections. This constitutes a significant difference between non-adiabatic processes involving three species and non-adiabatic atomic collisions; in the latter case the differential cross-section depends only on a single parameter (the impact parameter), which bears a single-valued (sometimes two-valued or three-valued) relation to the scattering angle[20]. Thus, whereas in the theory of non-elastic atomic collisions the main difficulty of the calculation of the cross-sections consists of the calculation of the transition probabilities, in molecular collisions the main problem involves the investigation of the motion of the system in the adiabatic regions of the configuration space.

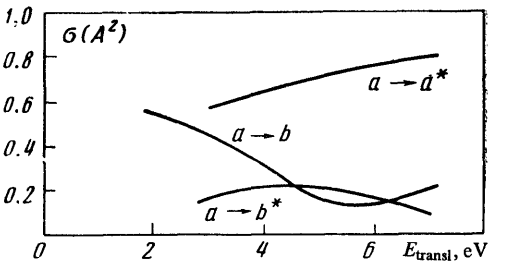


Figure 8. Variation of the cross-sections for reactions (16) with energy.

Another important difference between molecular non-adiabatic processes and atomic processes is that the vibration energy (and not the translational energy) can effectively induce transitions in molecular processes. With the potential energy surfaces for the H_3^+ ion, this is particularly clearly demonstrated by the calculation on the competition between the exchange and charge-transfer reactions[69]:

$$H + D_2^+ \begin{cases} \nearrow DH^+ + D \\ \searrow D_2 + H^+ \end{cases} . \qquad (17)$$

In this process the trajectory begins from the upper half of the pathway followed by the reactants (Fig. 7) subject to the condition that D_2^+ has undergone fairly intense vibrational excitation. Otherwise the trajectory of the reactants is not shown in Fig. 7 at all and their mutual approach, resulting in a transition from the diabatic to adiabatic D_2^+ vibrations, completely prevents the transition from the higher (dashed line) to the lower surface. Thus the probability of charge transfer, described by the transition of the system from the upper half of the reactant valley to the lower half, depends critically on the degree of vibrational excitation of D_2^+. The exchange process can proceed either adiabatically via singlet and triplet excited energy surfaces adjoining the D_2^+ diabatic terms in the initial process or via a non-adiabatic pathway along the lowest surface. In the first pathway it is necessary to overcome an energy barrier, which is not present in the second, but the latter includes a non-adiabatic transition. The competition between these possible processes determines ultimately the efficiency of the exchange.

Reactions Proceeding with a Change in Total Spin

If the set of the possible total spins of the reactants does not include any of the possible values of the total spin of the products, then the spin state of the system necessarily changes along the reaction pathway. The converse assertion is in general not valid: even if the

reaction satisfies Wigner's rule, the most effective reaction pathway need not necessarily correspond to an unchanged spin. An example of the latter process may be provided by the exothermic ion-molecule reaction

$$O^+(^4S) + N_2(^1\Sigma_g) \rightarrow NO^+(^1\Sigma) + N(^4S), \qquad (18)$$

which formally satisfies Wigner's rule.

In contrast to the majority of exothermic ion-molecule reactions, which usually proceed with large cross-sections and at low kinetic energies, the cross-section of reaction (18) is small for low energies and increases sharply with increase of E_{transl} and E_{vibr}. These features of the reaction can be understood qualitatively on the basis of correlation diagrams of electronic states (Fig. 9).

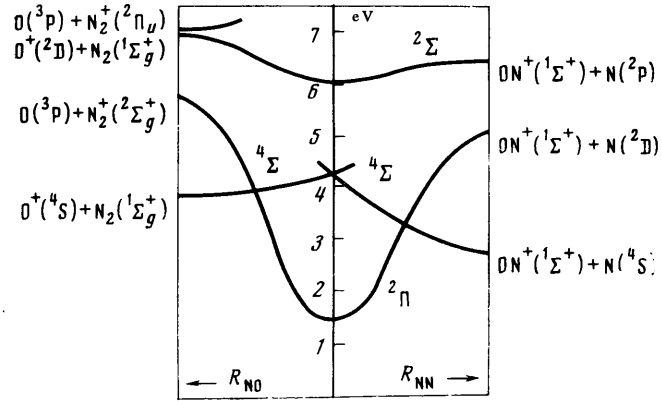


Figure 9. Correlation diagram for the electronic terms of the reaction $O^+ + N_2 \rightarrow NO^+ + N$.

The absence of activation energy in ion-molecule reactions is usually attributed to the fact that the repulsion of reactants due to the exchange interaction is fully compensated by polarisation attraction. However, if the repulsion is sufficiently marked, it can lead to a barrier even against the background of a strong polarisation interaction. Precisely this situation occurs in reaction (18). A non-empirical calculation of the cross-sections of the energy surfaces for the NNO^+ system has indeed shown[70] that in the initial and final pathways with a linear configuration the initial reactants and products repel one another ($^4\Sigma^-$ states). Possibly these two states are interconverted at short interatomic distances. The trajectory along the reaction pathway in an adiabatic mechanism (Fig. 9) requires that an activation barrier be overcome. The non-adiabatic pathway $^4\Sigma^- \rightarrow {}^2\Pi \rightarrow {}^4\Sigma^-$, in which the multiplicity of the system changes twice, can in principle compete with the above pathway. In this reaction mechanism the increase of the cross-section with the energy in the region of low energies can be explained by the existence of a small potential barrier at the point of intersection of the $^4\Sigma^-$ and $^2\Pi$ states in the initial pathway. After the N_2O^+ system has passed to the bonding state $^2\Pi$, it decomposes almost exclusively to the final state by a non-adiabatic transition at another point of intersection of the $^2\Pi$ and $^4\Sigma^-$ states[70].

With increase of the energy, the attainment of the region of the quasi-intersection of the $^4\Sigma^-$ states becomes possible. In this region the increase of the cross-section can be simply related to the increase of the transition probability with increase of E_{transl} and E_{vibr}. A rational calculation of the probability is possible only when the dynamic problem is solved. Since, however, the surface in this region is unknown, O'Malley[71] suggested that the system follows mainly the diabatic states and that the transition probability can be estimated by means of the first order perturbation theory in terms of the interaction corresponding to the quasisplitting. The change in the NN bond length is treated as the coordinate of the diabatic motion. In this case the profile of the reaction pathway has the form of a parabolic potential (the initial diabatic term corresponding to the N_2 vibrations), which is intersected by a monotonically decreasing potential (the final diabatic term describing the relative motion of N and NO^+) (Fig. 10). Within the framework of this one-dimensional model, the reaction probability $P(E_{\text{transl}}, E_{\text{vibr}})$ is proportional to the square of the overlap of the vibrational eigenfunctions and the wavefunctions for the continuous spectrum. For very low (thermal) energies, the overlapping of the functions of the vibrational ground state and those of the continuous spectrum is so slight that the entire diabatic mechanism is masked by the non-adiabatic mechanism $^4\Sigma^- \rightarrow {}^2\Pi \rightarrow {}^4\Sigma^-$.

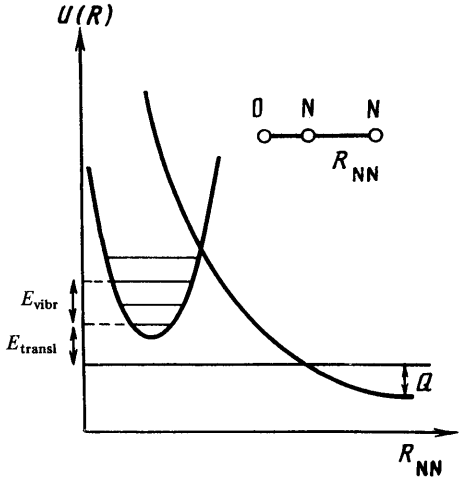


Figure 10. Illustration of the non-adiabatic mechanism of the reaction $O^+ + N_2 \rightarrow NO^+ + N$.

With increase of E_{vibr}, the overlapping will also increase and this is reflected in a sharp increase of the cross-section as a result of the contribution of the diabatic mechanism. On the other hand, the overlapping also increases with increase of E_{transl}. In the ground vibrational state, the cross-section reaches a maximum for values of E_{transl} such that the parabolic term intersects the repulsive term in the region of the minimum of the former. Finally, for a fixed E_{transl}, this mechanism predicts a less marked increase of the cross-section with

increase of E_{vibr} the higher the value of E_{transl}. All these conclusions, based on a simple model, were confirmed experimentally[72,73], which throws doubt on the adiabatic direct dislodgement mechanism put forward by Golubkov and Ivanov[74].

The mechanism of reaction (18) discussed above makes it possible to understand why the isotope exchange reaction

$$N'(^4S) + N_2(^1\Sigma_g) \rightarrow N'N(^1\Sigma_g) + N(^4S)\,, \qquad (19)$$

which is isoelectronic with reaction (18), occurs very slowly if at all[75]. Despite the existence of the stable complex N_3, transition to the latter is probably forbidden by the spin. On the other hand, isotope exchange reactions such as

$$\begin{aligned} O' + O_2 &\rightarrow OO' + O\,, \\ O' + CO &\rightarrow CO' + O \end{aligned} \qquad (20)$$

are very rapid: the first proceeds on the singlet surface of the O_3 ground state and the second on the triplet surface of CO_2. In many cases, for example for the reaction

$$N + NO \rightarrow N_2 + O\,, \qquad (21)$$

it is at present still impossible to interpret the mechanism unambiguously in view of the competition between the adiabatic and non-adiabatic pathways[76]. In general one may expect that, in reactions involving C, N, and O atoms and ions, non-adiabatic mechanisms should be extremely common (see, for example, Tully et al.[77] in connection with the reaction $N^+ + O_2 \rightarrow NO^+ + O$).

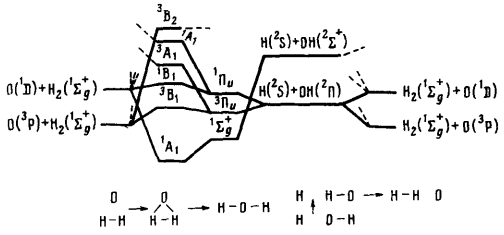


Figure 11. Correlation diagram for the electronic states of the reaction $O + H_2 \rightarrow OH + H$.

A dependence of the rate constant on the spin–orbit interaction in a number of similar reactions might constitute direct proof of a non-adiabatic mechanism infringing Wigner's rule. Unfortunately the activation energy also varies in many such series, so that it is fairly difficult to isolate the pure effect of the spin–orbit interaction. A reaction of the type

$$O(^3P) + HX(^1\Sigma) \rightarrow OH(^2\Pi) + X(^2P)\,, \qquad (22)$$

where X = Cl, Br, or I atoms, may be quoted as the only example which probably indicates the involvement of spin–orbit interaction[78]. Although formally there exists an adiabatic pathway along a triplet surface for these reactions, the correlation diagram for the states shows[79] that in the case of the non-linear configuration OHX the singlet surface lies below the triplet surface on the product side and the preferred reaction pathway at low temperatures involves a transition from the triplet surface $^3A'$ to the singlet surface $^1A'$. The transition probability for a fairly weak spin–orbit interaction is proportional to the square of the perturbation, which is determined by the fine splitting of the $^2P_{1/2}$ and $^2P_{3/2}$ states of the atoms X.[79] Thus the theory predicts a quadratic increase of the pre-exponential factor with increase of the splitting of the ^2P state, which is in qualitative agreement with experiment. For a more detailed investigation of the mechanism of reactions (22), it is necessary to have information about the details of the potential energy surfaces.

From this standpoint, the most complete information is available about the energy surfaces for the $O(^3P)$, $O(^1D) + H_2(^1\Sigma_g^+)$ system[80,81] (Fig. 11).

The study of the possible reaction pathways has shown that, although in the linear configuration the abstraction reaction

$$O(^1D) + H_2(\Sigma_g^+) \rightarrow OH(^2\Pi) + H(^2S) \qquad (23)$$

has a comparatively high activation energy (about 25 kcal mole^{-1}), there is probably no barrier for non-linear collisions. This instance of abstraction can be represented as decomposition of the vibrationally excited H_2O molecule in its ground electronic state, formed when $O(^1D)$ is inserted in the H–H bond. On the other hand, the abstraction reaction on the triplet surface,

$$O(^3P) + H_2(^1\Sigma_g^+) \rightarrow OH(^2\Pi) + H(^2S) \qquad (24)$$

has a potential barrier for all the configurations. If the $O(^3P) + H_2$ system reaches the line of intersection of the triplet and singlet surfaces before the region of the saddle point on the triplet surface, then, providing there is a fairly high transition probability, reaction (24) would occur without a change in spin. However, this probability is low for the H_2O molecule, as shown, in particular, by studies on the reaction

$$O^+(^4S) + H_2(^1\Sigma_g^+) \rightarrow OH(^2\Pi) + H^+ \qquad (25)$$

in molecular beams[82]. It has been found that reaction (25) proceeds via the direct mechanism, i.e. the H_2O^+ complex is not formed in the ground electronic state (Fig. 12).

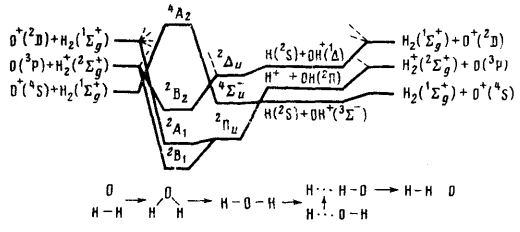


Figure 12. Correlation diagram for the electronic states of the reaction $O^+ + H_2 \rightarrow OH + H^+$.

For reactions involving heavier atoms, the spin–orbit interaction can be sufficiently strong to induce transitions between surfaces of different multiplicity [as happens in reaction (22)]. In this connection we may point to the reaction

$$O(^3P) + Br_2(^1\Sigma) \rightarrow OBr(^2\Pi) + Br(^2P)\,, \qquad (26)$$

which was recently investigated by the molecular beam method[83]. The angular and energy distribution of the

products shows that the reaction proceeds via the formation of the long-lived complex OBr_2. However, this complex can be formed only in its singlet state, so that the dynamic characteristics of the reaction show directly that the mechanism is non-adiabatic. A non-adiabatic mechanism should also be expected for reactions of excited oxygen atoms (see, for example, Pravilov and Vilesov's review[84]).

5. NON-ADIABATIC IMPACT DISSOCIATION

The impact dissociation of molecules BC in reaction (1) is understood as decomposition as a result of a single A + BC collision step. In this respect impact dissociation differs from thermal decomposition, which occurs as a result of many consecutive collisions of BC with the atoms or molecules of the heat reservoir. Many thermal non-adiabatic decomposition processes of triatomic molecules have now been studied[43] together with certain processes involving the thermal non-adiabatic decomposition of diatomic molecules into ions[85-87]. All these processes proceed via the stage of spontaneous non-adiabatic decomposition of an isolated molecule in the state which it attains after excitation. In this respect thermal non-adiabatic decomposition processes are analogous to processes involving spontaneous predissociation of molecules[88]: the only difference between them merely involves the excitation mechanism (by collision or by absorption of light), which has no direct bearing on decomposition.

In non-adiabatic impact dissociation the transitions take place between the potential energy surfaces of the system ABC and not between the terms of an isolated diatomic molecule BC, so that the excitation and decomposition cannot be treated independently.

Among all the non-adiabatic impact dissociation processes, the simplest is the predissociation of diatomic molecules induced by collisions. Molecules in an excited vibrational level of a bound excited electronic state, whose surface intersects that of the antibonding electronic state, usually undergo induced predissociation. If these states differ in parity or symmetry relative to reflection in the plane passing through the nuclei of BC, then spontaneous predissociation is impossible. Transitions between these states are induced by an external perturbation, which removes a corresponding symmetry operation of the Hamiltonian of an isolated molecule.

The induced predissociation of iodine in the $B^3\Pi(0_u^+)$ state has been investigated in greatest detail (see Mulliken[89] and the references quoted therein). The interpretation of the I_2 spectrum[89] and also non-empirical asymptotic calculations[90] yield the following pattern of states. The $0_u^+(B^3\Pi)$ state, which correlates with the $^2P_{1/2}$ and $^2P_{3/2}$ atomic states, is crossed by the $3_u(^3\Delta_u)$, $0_u^-(^3\Sigma_u^+)$, $0_g^+(^3\Sigma_g^-)$, $1_g(^3\Pi_g)$, and $2_g(^3\Pi_g)$ states on the side of the dissociation limit and by the $1_u(^1\Pi_u)$ and $0_u^-(^3\Pi_u)$ states on the side of the repulsive limb (all these states are correlated with the atomic states $^2P_{1/2}$ and $^2P_{3/2}$). The intersection with the 1_u state is responsible for the spontaneous dissociation of I_2 and the intersection with the states $0_u^-(^3\Sigma_u^+)$ and $0_u^-(^3\Pi_u)$ is responsible for the predissociation induced by the magnetic field; the intersection with the 0_g^+ state probably makes the main contribution to the predissociation induced by collisions. If it is supposed that the perturbing effect of the third particle reduces solely to the removal of the prohibition of the transition between the states†, which should now be regarded as diabatic from the standpoint of the classification adopted here, and that the transition probability is low, then the dissociation rate constant k should be correlated with the average parameter $2\pi a^2/\hbar|F_{1R} - F_{2R}|v_R$ in Eqn. (4). Calculations show that, for a fixed vibrational state of I_2, the constant k is proportional to $\alpha_A^2 R_0^{-9}$, where α_A is the polarisability of the other species A involved in the I_2 + A collision and R_0 is the gas-kinetic radius of the pair (in one of the earlier studies[92] it was erroneously suggested that k be correlated with the parameter $I_A\alpha_A\mu^{1/2}R_0^{-3}$). The available experimental results confirm this correlation.

However, this type of treatment is not sufficiently general, since no account is taken of the perturbing effect of the A species on the motion of the I atoms. Allowance for this perturbing effect in fact implies the solution of the dynamic three-particle problem, which was recently investigated within the framework of the classical[93] and semiclassical[94] approximations without taking into account non-adiabatic transitions.

Whereas the phenomenon of induced predissociation has been known for a comparatively long time, the study of non-adiabatic impact dissociation of molecules, which are in the lowest vibrational states before collision, is only just beginning. These processes include the dissociation of the salts NaBr,[95] CsI,[96] and TlX [97,98] (X = halogen atom) into ions in collisions with inert gas atoms and also the dissociation of the molecules X_2 in collisions with caesium[99] and potassium[100-103] atoms. The competition between the different possible non-adiabatic channels was also investigated for the latter processes[102,103]:

$$\mathrm{M} + \mathrm{XY} \begin{cases} \nearrow \mathrm{M^+ + XY^-} \\ \rightarrow \mathrm{M^+ + X + Y^-} \\ \searrow \mathrm{M^+ + X^- + Y}, \end{cases} \qquad (27)$$

(here M is an alkali metal atom and X and Y are halogen atoms). For relative kinetic energies exceeding the thresholds of the chemi-ionisation processes (27), these channels are the main ones and the competing exchange association processes involving the formation of neutral products,

$$\mathrm{M} + \mathrm{XY} \begin{cases} \nearrow \mathrm{MX + Y} \\ \rightarrow \mathrm{MY + X} \\ \searrow \mathrm{M + X + Y}, \end{cases} \qquad (28)$$

are comparatively ineffective. The main characteristics of the dynamics of reaction (27) and (28) can be explained qualitatively by the electronic harpooning mechanism[1]. Within the framework of this concept, two functions of the rough adiabatic basis—the function of the covalent state ψ_c (M + X_2 system) and the function of the ionic state ψ_i ($M^+ + X_2^-$) system‡—are adduced in the description of the reaction. Two potential energy surfaces correspond to these wavefunctions—the covalent (U_c) and ionic (U_i) surfaces. If the energy of the unbound system M + X + X is adopted as the starting point of the calculation, then, for large distances R between M and the centre of gravity of XX, the potentials U_c and U_i are

$$U_c = c(r, \gamma)/R^6 + \ldots$$
$$U_i = [I_M - A_{X_2}(r)] - e^2/R + \ldots \qquad (29)$$

† In terms of this approximation, the induced predissociation of diatomic molecules is analogous to the radiationless transitions induced by collisions in polyatomic molecules[91].

‡ For simplicity, the case where X = Y will be considered henceforth.

(where r is the internuclear distance in XX, γ is the angle between the vectors **r** and **R**, and $A_{X_2}(r)$ is the electron affinity of XX). The U_c and U_i surfaces intersect along a line given by the following equation when all interactions other than Coulombic are neglected:

$$e^2/R = I_M - A_{X_2}(r) \ . \qquad (30)$$

If account is taken of the interaction between the covalent and ionic states, the intersection is replaced by a quasi-intersection, so that the line defined by Eqn. (30) gives the location of the region of the possible non-adiabatic coupling. The minimum splitting between the states is equal to twice the matrix element of the interaction

$$V_{ic} = C(R, r, \gamma)\exp[-(A_{X_2}(r)/I_n)^{1/2} \cdot R/a_0]\cos^2\gamma \ . \qquad (31)$$

The variation of V_{ic} with the coordinates is specified mainly by the last two multipliers of this expression, which depend on their arguments to a greater extent than does the coefficient $C(R_r, \gamma)$.[104] A characteristic feature of the interaction is the equality of V_{ic} to zero when $\gamma = \pi/2$, i.e. when MX_2 has the configuration of an equilateral triangle. This corresponds to the familiar case of the conical intersection of the states[4,7].

In the products channel the interaction between the states rapidly attains its asymptotic value corresponding to the interaction of the covalent and Coulombic states of an isolated molecule. In terms of the coordinates R_{MX} and R_{XX}, the line of the quasi-intersection in the products channel,

$$R_{MX} = R^0_{MX} \ , \qquad (32)$$

on which the splitting of the adiabatic terms is constant, becomes straight.

In the region of strong interaction of all three particles, the line of the quasi-intersection, defined by Eqn. (30), is continually converted into the straight line defined by Eqn. (32). The position of this line and the general characteristics of the two lowest U_c and U_i surfaces for the collinear configuration of the M + X + X atoms are illustrated in Fig. 13. As in the previous Figures, the inserts show the cross-sections of the lowest (continuous lines) and highest (dashed line) adiabatic surfaces. The quasi-intersection line is represented by a continuous curve in the output channel in conformity with the fact that, for energies such that chemi-ionisation is possible, the system in this channel is characterised by diabatic behaviour (the trajectory of the representative point does not cross the continuous line). In the initial channel, part of this line is shown dashed (there is an appreciable probability of adiabatic motion of the system), which when produced yields the limit of the sharp descent on the adiabatic surface. In this region non-adiabatic transitions are unlikely, since the splitting of the states is large.

Various approximations for the description of the energy surfaces of the ground state of the MXX system are now known[105-108] and also semiempirical[109] and non-empirical calculations have been made for the simple LiFF system[110,111].

The dynamics of adiabatic reactions (28) was investigated in a series of studies with an exact solution of the classical dynamic problem[105-108,112], as well as within the framework of simplified approaches[113,114]. The qualitative dynamic pattern corresponds to the vertical transition $X_2(r) \rightarrow X_2^-(r)$ in the field of the ion M^+ retained in the vicinity of X_2^- by Coulombic attraction ("the electron harpoon"). The stripping mechanism with participation of the spectator[1], which was proposed in earlier investigations and was shown by subsequent investigations, not to be fully justified, constitutes the limiting simplification of the mechanism described above.

The relevant studies on the dynamics of non-adiabatic reactions (27) are only just beginning. Important information about the variation of the adiabatic terms can be derived from the study of non-elastic and atomic collisions accompanied by the formation of ions[115-117]:

$$M + X \rightarrow M^+ + X^- \ . \qquad (33)$$

In particular the matrix element for the interaction between the ionic and covalent terms[116], which determines the oscillatory structure of the differential cross-section of reaction (33), can be estimated in this way. The interpretation of the differential cross-section of the reaction involving charge transfer to the molecule [the first reaction (27)] is more difficult, since it is then necessary to take into account the effect of the rotation and vibration of the molecule X_2. It is found that the characteristics of the differential cross-sections can be understood if rotation alone is taken into account[118].

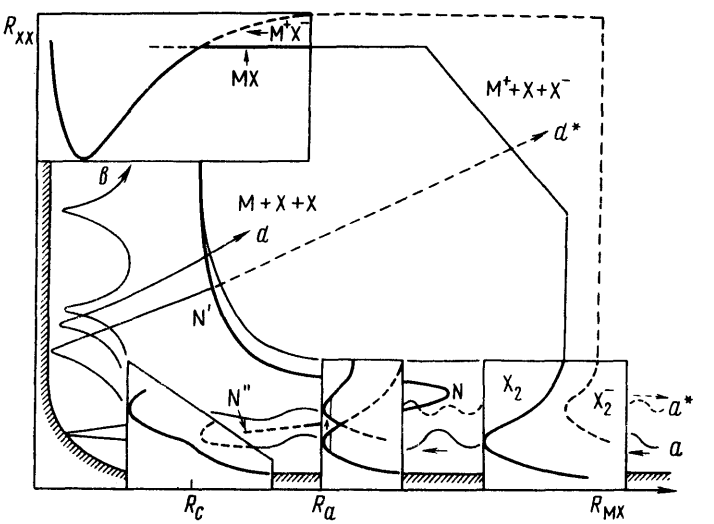


Figure 13. Schematic illustration of the potential energy surface for the collinear system MX_2.

However, the energy dependence of the total charge-transfer cross-section near the threshold depends significantly on the vibrations of X_2. The experimental threshold for the formation of the ion is equal to the difference between the ionisation potential of M and the adiabatic electron affinity A_a of the molecule X_2. This is at first sight inconsistent with the hypothesis of the vertical transition $X_2 \rightarrow X_2^-$ leading to the formation of ions subjected to a strong vibrational excitation. The non-vertical transition corresponding to the affinity A_a also corresponds to the transition between the potential minima of X_2 and X_2^-. This is possible, for example, as a result of tunneling between two potential wells (the potentials of the X_2 and X_2^- vibrations) for distances between the reactants such that the energy levels of the ground vibrational states in the diabatic potentials of the molecule and ion are the same. This transition, occurring when $R \simeq R_a$,

is indicated by an arrow in Fig. 13. Its probability is proportional to the Franck-Condon factor $S_{00}[X_2(v = 0) \rightarrow X_2^-(v = 0)]$ and determines the cross-section directly above the threshold. The energy dependence of the cross-section should be correlated with the variation of the overlap integrals S_{0v} with the number v of the vibrational level of X_2^-, which may be excited on electron transition[119].

However, it is possible to put forward also another mechanism to account for the threshold variation of the cross-section[120-121]. According to this mechanism, involving the classical approximation, the trajectory follows the minimum in the reactant valley (the initial trajectory a), reaching a sharp break in the states at $R \simeq R_C$ in the region of the quasi-intersection of the covalent and ionic states [the coordinate of the break R_C corresponds to the vertical transition $X_2 \rightarrow X_2^-$ when the reactants approach one another, and is determined from Eqn. (30) in which one must put $r = r_e$]. After reaching the break, the trajectory corresponds to the extension of the bond in the ion X_2^-, i.e. to the onset of dissociation of the ion. However, before this process reaches completion the collision of M^+ with one of the atoms of X_2^- leads to marked deactivation of X_2^- as a result of which the ion loses energy and M^+ is strongly accelerated. The ion M^+ begins to move along the reactant valley in the opposite direction and can intersect the line N'NN" of the quasi-intersection of the surfaces in the region where the motion is almost diabatic. The final result of such collision (the trajectory a^* corresponding to the highest state) is the formation of the ions M^+ and X_2^-, the reaction threshold being determined by the adiabatic electron affinity of X_2 despite the fact that the electron transition is a vertical process. This mechanism predicts a correlation between the energy dependence of the cross-section and the probability of the deactivation of the ion X_2^- on collision with M^+ as a result of the brief exchange interaction. Naturally, elucidation of the true mechanism of the formation of ions requires a more thorough investigation of the collision dynamics.

With increase of the energy above the molecular ion formation threshold, the atomic ion formation threshold is reached. One of the trajectories (trajectory d^*) leading to such products is illustrated in Fig. 13. The velocity along the quasi-intersection line N'N is so high that the probability of the non-adiabatic transition is close to unity. Under these conditions, the formation of neutral atoms in adiabatic dissociation (trajectory d) and of neutral molecules in adiabatic exchange (trajectory d) is unlikely.

Possibly a large number of surfaces must be adduced in order to refine further the mechanism of such reactions. This is indicated by the results of a study of processes involving the formation of the products $X + Y^-$ and $X^- + Y$ in reaction (27).[103] Moreover, if one is dealing with impact dissociation under the influence of an inert atom (for example the reaction $TlCl + Ar \rightarrow Tl^+ + Cl^- + Ar$), then it is absolutely essential to take into account several potential surfaces for a correct interpretation of the experimental results.

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