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Non-adiabatic Processes of Energy Transfer in Gases

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The present review examines general methods for constructing the adiabatic electronic functions of molecular systems produced by binary collisions of atoms and molecules in gases. Mechanisms of energy transfer accompanying the collision of electronically excited atoms and molecules are discussed on the basis of the selection rules for non-adiabatic interactions and models of non-adiabatic coupling. These mechanisms are classified according to the amounts of electronic energy transferred on collision and according to the distances at which transfer takes place between the electronic states of the colliding species. The quenching of the electronically excited states of the atoms is brought about by close approach of the colliding species, and the probability of transitions and the corresponding cross-section depend in decisive fashion on the characteristics of the electronic functions of the system of two interacting species. Transitions between the components of the fine structure of the atomic terms take place at large distances, and the cross-section can be interpreted in terms of the characteristics of the non-excited functions for the interacting species. Transitions between the vibrational levels of molecules with incomplete electronic sub-levels are determined by vibronic or spin-orbital interaction in a given electronic configuration. The bibliography contains 62 references.

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INTRODUCTION

The recent progress in theoretical and experimental studies of elementary processes in the gaseous phase makes possible a detailed interpretation of the mechanisms of molecular collisions leading to energy exchange and to redistribution of the particles. Many processes take place through excited electronic states and their description requires introduction of the theory of non-adiabatic transitions. The present paper examines various processes of energy transfer involving atoms and diatomic molecules under the conditions in which the kinetics of reactions in the gaseous phase are usually studied. These processes are also used to illustrate the achievements of the theory of non-adiabatic processes.

Mention must be made of two characteristic features of molecular collisions under the above conditions. These characteristic features are extremely important, since they make it possible to simplify the overall problem considerably. On the one hand, the energy of the colliding species is so low that in the calculation of the cross-section or rate constant it is possible to consider only a small number of electronic states. On the other hand, the motion of the nuclei can still be treated quasi-classically, and very often an analysis of the classical trajectories is sufficient for the calculation of the redistribution of energy and the probability of transition between closely situated electronic terms.

1. ADIABATIC BASIS

The original approximation in the examination of the process of electronic energy transfer on slow collisions is the adiabatic approximation. There are two ways of constructing the adiabatic electronic basis: one involves the solution of the electronic wave equation for an arbitrary nuclear configuration R, whereas the other involves the solution of the equation for a configuration R_0 fixed in definite fashion[1]. Following Longuet-Higgins[2], we shall call these two possibilities the adiabatic approximation and the simple adiabatic approximation. The construction of the two bases is shown in Table 1. Here $t(r)$ and $T(R)$ denote the electronic and nuclear kinetic energy operators, $V(r, R)$ the electronic–nuclear interaction, H the complete Hamiltonian, and H_{el}, H_{nucl}, H^0_{el}, and H^0_{nucl} the partial Hamiltonians encountered in intermediate stages. Between these two limiting cases there is a whole series of other possibilities corresponding to the partitioning of the potential $V(r, R)$. For example, the usual approximation used in the calculation of the electronic structure of molecules involves making allowance for only the electrostatic contribution $V_{el}(r, R)$ to $V(r, R)$ with complete neglect of the spin-orbital interaction $V_{s.o}$. The corresponding electronic wave functions $\varphi'_n(r, R)$, which can be called the adiabatic functions of the zeroth approximation, depend parametrically on R, but the coupling between them is due not only to the operator $T(R)$ (as in the adiabatic approximation), but also to the interaction $V_{s.o}$ (as in the simple adiabatic approximation).

The exact electronic-nuclear function $\Psi_\epsilon(r, R)$ can be expanded into a series for any set, but the unknown amplitudes $A_{nE}(R)$ and $B_{nE}(R)$ must be found from an infinite system of related equations. Termination of the system, leading to the so called approximation of N-states, will generally speaking give different approximations for the complete function Ψ_ϵ in the adiabatic basis and the simple adiabatic basis. If, however, the main contribution is made only by several electronic states, the partitioning of V into V_0 and δR in appropriate fashion often makes it possible to obtain almost identical results for any basis set. This means that the N functions $\varphi_n(r, R)$ and the N functions $\varphi^0_n(r, R)$ can be regarded to a good approximation as complete sets of functions corresponding to the problem

being considered (the first simplification mentioned in the introduction).

The semi-classical approach to Ψ^a and $\Psi^{0,a}$ is obtained by replacing the nuclear functions by time-dependent exponential terms, where the classical trajectory of the nuclei is introduced $R = R(t)$ (Table 2). The choice of trajectory is a difficult problem, since it should effectively give the motion of the nuclei over several potential surfaces at once (at least in the region of strong coupling). If, however, it is possible to restrict the examination to several closely situated electronic terms, it is possible to formulate a reasonable approximation for $R(t)$ (second simplification mentioned in the introduction).

Table 1. Construction of adiabatic basis.

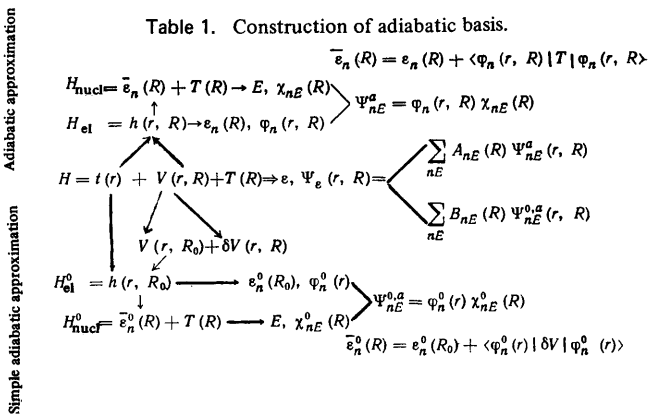


Table 2. Semi-classical approximation and non-adiabatic coupling.

Semi-classical approximation	$\Psi^a_{nE}(r, R) = \varphi_n(r, R)\chi_{nE}(R) \to$ $\to \Psi^a_n(r, R(t)) = \varphi_n(r, R(t)) \times$ $\times \exp\left[-\frac{i}{\hbar}\int_{R=R(t)}^{t} \bar{\varepsilon}_n(R)\,dt\right]$,	$\Psi^{0,a}_{nE}(r, R) = \varphi^0_n(r)\chi^0_{nE}(R) \to$ $\to \Psi^{0,a}_n(r, R(t)) = \varphi^0_n(r) \times$ $\times \exp\left[-\frac{i}{\hbar}\int_{R=R(t)}^{t} \bar{\varepsilon}^0_n(R)\,dt\right]$
Non-adiabatic coupling	$\hat{C}_a = i\hbar\frac{\partial}{\partial t} = i\hbar v(t)\frac{\partial}{\partial R}$	$\hat{C}^0_a = \delta V[R(t)]$
Non-adiabatic wave function	$\Psi(r, t) = \sum_n A_n(t)\Psi^a_n(r, R(t))$, $i\hbar A_n = \sum_m \left\langle \varphi_n \middle\| i\hbar\frac{\partial}{\partial t}\middle\| \varphi_m \right\rangle \times$ $\times \exp\left[-\frac{i}{\hbar}\int [\bar{\varepsilon}_m - \bar{\varepsilon}_n]\,dt\right] A_m$	$\Psi(r, t) = \sum_n B_n(t)\Psi^{0,a}_n(r, R(t))$, $i\hbar B_n = \sum_m \langle\varphi^0_n|\delta V|\varphi^0_m\rangle \times$ $\times \exp\left[-\frac{i}{\hbar}\int [\bar{\varepsilon}^0_m - \bar{\varepsilon}^0_n]\,dt\right] B_m$

We shall not discuss here the problems associated with the calculation of the adiabatic electronic terms, and we shall mention only various useful approximations. If a comparatively large amount of electronic energy is converted into vibrational, rotational, and translational energy, the non-adiabatic coupling is usually localised at small intermolecular distances, and some information from *a priori* calculations of states is necessary. If the energy of the electronic transition is small, the interaction between the electronic terms generally takes place at large distances, and various asymptotic methods for calculating the terms can be used[3-6]. Moreover, a number of semi-empirical methods of estimating potentials, analogous to the methods used in the calculation of the probabilities of vibrational transitions[7], often prove useful.

2. NON-ADIABATIC COUPLING AND THE SELECTION RULES

The semi-classical adiabatic states corresponding to the functions Ψ^a_{nE} and $\Psi^{0,a}_{nE}$ are coupled by an interaction which was omitted in the derivation of H_{nucl} and H^0_{nucl}. The coupling operators and the semi-classical equations for the amplitudes $A_n(t)$ and $B_n(t)$ are given in Table 2. The differential equations should be integrated along the chosen trajectory, so that $\Psi_\varepsilon(r, t)$ gives the time development of the electronic functions along this trajectory. At a distance from the region of non-adiabatic interaction, $A_n(t)$ tend to constant values, and at a distance from the interaction region due to the potential δV the coefficients $B_n(t)$ also tend to constant values. These constant values of the probability amplitudes make it possible to find the system in the electronic states φ_n or φ^0_n.

In the region of non-adiabatic coupling, definite selection rules are obeyed by the electronic quantum numbers n and n'. These can be readily obtained by writing the operator C in terms of the elementary relative displacements and rotations of the axes of the system as a whole. A summary of the selection rules for a system of two colliding atoms is given in Table 3 in terms of the usual symbols[8]. Here Ω is the projection of the total momentum of the electrons on the molecular axis $\Omega = \Lambda + S_z$, and Λ and S_z are the projections of the angular momentum and the spin. The signs + and − for the Σ terms correspond to the sign on reflection of the spatial part of the wave function in a plane containing the molecular axis, and the same signs for the terms of $\Omega = 0$ correspond to the behaviour on reflection of the complete function (spatial and spin parts), whose construction made allowance for spin-orbital interaction. In this classification, for example, the ground state $^3\Sigma^-_g$ of the O_2 molecule can also be written in the form of the doublet $1_g 0^+_g$.

Table 3. Adiabatic quantum numbers and non-adiabatic selection rules for a system of two atoms.

Zeroth adiabatic approximation		Adiabatic approximation	
Perturbation: spin-orbital interaction +		radial and tangential movement of nuclei	
S	$\Delta S = \pm 1$		
S_z	$\Delta S_z = \pm 1$	Ω	$\Delta\Omega = 0\,(z)$
Λ	$\Delta\Lambda = \pm 1$ $\Big\}\ \Delta\Omega = 0$		$\Delta\Omega = \pm 1\ (R_x)$
g, u	conserved	g, u	conserved
Σ^+, Σ^-	$\Sigma^+ \longleftrightarrow \Sigma^-$	$0^+, 0^-$	$0^+ \leftarrow\!\!\!|\!\!\!\rightarrow 0^-$

For an arbitrary triatomic system, there is only one obvious adiabatic quantum number—the nature of the reflection of the electronic function in a plane of symmetry. Any motion in the plane leaves it unchanged; this is analogous to the preservation of the sign + or − for the state of a diatomic system, when the fixed plane coincides with a

plane normal to the vector of the relative angular momentum of the nuclei. Rotation of the plane of the triatomic system will induce a change in the sign + or −, leading to mixing of all the states.

For the special case of the collision of an atom with a diatomic molecule with identical nuclear charges, it is possible to introduce a more useful classification of states, if the main contribution to the non-adiabatic coupling is made by the region where the configuration of the nuclei corresponds to C_{2v} symmetry. In this case the symbols of the irreducible representations of this point group serve as adiabatic quantum numbers. The irreducible representations and the corresponding characters are given in Table 4 for the one-dimensional representations (systems with integral spin) and two-dimensional representations (systems with half-integral spin). Here E denotes the identity operator, C_z rotation about the axis of symmetry, σ rotation in the plane of the atoms, and σ' rotation in another plane of symmetry, perpendicular to the first. Q denotes rotation by 2π, which for the two-dimensional representations is regarded as being different from E. The system of coordinates x, y, z is chosen in such a way that the z axis is directed along the axis of symmetry, and the x axis is perpendicular to the plane of the atoms.

Table 4. Adiabatic quantum numbers (irreducible representations and their characters) for a system of three atoms.

Group C_2					Group C_s		
One-dimensional representations	E	C_2	σ_v	σ_v'	One-dimensional representations	E	σ_v
$A_1(z)$	1	1	1	1	$A'(y, z, R_x)$	1	1
$B_2(y, R_x)$	1	−1	1	−1			
$A_2(w = xy, R_z)$	1	1	−1	−1	$A''(x, R_y, R_z)$	1	−1
$B_2(x, R_y)$	1	−1	−1	1			
Two-dimensional representations	E	Q	C_2, C_2Q	σ_v', $\sigma_v'Q$	σ_v'', $\sigma_v''Q$	Two-dimensional representations	E	Q	σ_v, σ_v, Q
$E''\begin{pmatrix}\alpha\\ \beta\end{pmatrix}$	2	−2	−0	0	0	$E''\begin{pmatrix}\alpha\\ \beta\end{pmatrix}$	2	−2	0

Table 5. Non-adiabatic selection rules for a system of three atoms.

C_s		A'		A''	
	C_{2v}	A_1	B_1	A_2	B_2
A'	A_1	z	z, y R_x	R_z	R_y
	B_1	z, y R_x	z	R_x	R_z
A''	A_2	R_z	R_x	z	z, y R_x
	B_2	R_y	R_z	z, y R_x	z

It can be seen from Table 4 that there are no special selection rules for systems with half-integral spin. This is related to the fact that, of the two components of the Kramers doublet, one always has the proper symmetry. If the spin-orbital coupling is weak and can be regarded as a perturbation in the adiabatic basis of the zeroth approximation, the classification of states can be carried out in accordance with the one-dimensional representations of the point groups C_{2v} and C_s. The selection rules for the groups C_{2v} and C_s are summarised in Table 5. For C_{2v} symmetry the operation z denotes any movement of the nuclei in the fixed plane, preserving this symmetry, y represents any other movement in the fixed plane, R_z represents rotation about the axis of symmetry, R_x rotation in the fixed plane, and R_y a third rotation, affecting the orientation of the plane of the atoms in space. For C_s symmetry the operations z and y denote any movement in the plane (z and y can be pictured as the radial and tangential relative movement of the interacting species), R_x represents rotation in the fixed plane, and R_z and R_y two rotations of the plane of the atoms. The spin-orbital interaction (if it has not already been taken into account and is regarded as a perturbation) couples all the states.

These selection rules may be used below to discuss the simple elementary processes in which non-adiabatic effects are significant.

3. MODELS OF NON-ADIABATIC COUPLING

After the selection rules have been elucidated and the equations written, the problem reduces to the solution of these equations. The rapid development of electronic computers is simplifying this stage continuously. Simple models which permit an analytical solution are still playing a fundamental part, however, at least in the physical understanding of the non-adiabatic interaction of electrons and nuclei. There are a number of general approaches to the calculation of the probabilities of non-adiabatic transitions. They are all based on the application of perturbation theory either with respect to C or with respect to C^0 (Table 3).[8] If the perturbation is not small, the approximation of strong coupling, that is exact solution of a terminated system of equations, gives best results.

Of the strong coupling approximations, the so called approximation of two states is most widely used. The corresponding models are conveniently classified according to the functional dependence of the expressions adopted for the approximations $\overline{\epsilon}_1^0$ and $\overline{\epsilon}_2^0$, and also of the non-diagonal matrix element δV_{12} in the basis of the two functions φ_1^0 and φ_2^0 of the simple adiabatic approximation.

With this classification we can discuss three main types of model.

a. The linear model, in which the matrix elements in the non-adiabatic region are approximated by linear functions of the nuclear coordinates. This model was first formulated by Landau[9] and Zener[10]. Subsequent studies, published chiefly in the last five years, have extended the range of applicability of this model both for the wave description of the motion of nuclei[11-15] and for the classical description[16-19].

b. The exponential model, in which the matrix elements are approximated by exponential functions of the nuclear coordinates. The most general formulation within the framework of the semi-classical approximation was made in a paper by Nikitin[20], which yielded, in particular, the results obtained by Rosen and Zener[21], who were the first to examine the exponential model. This model was subsequently developed further[22-24].

c. The power model, in which the matrix elements are approximated by power functions of the internuclear distance R^{-n} or R^{n}. This model has been studied comparatively recently[25-27].

Finally, mention must be made of papers[28-34] in which general aspects of the theory of the non-adiabatic coupling of two states are discussed.

All the elementary processes discussed below can be related to the various models, which in turn make it possible to interpret the cross-sections or rate constants of the non-adiabatic characteristics of the interacting species.

4. TRANSFER OF LARGE AMOUNTS OF ELECTRONIC ENERGY

A simple example of the exchange of energy between electronic and translational degrees of freedom is provided by the thermal excitation and deactivation of alkali metal atoms M on collision with atoms of an inert gas X

$$M(^2S) + X(^1S_0) \rightleftarrows M^*(^2P_j) + X(^1S_0) - \Delta\varepsilon \quad . \qquad (1)$$

An early interpretation of the quenching of the fluorescence of sodium by argon[35] was based on a simplified version of the theory and was related to low-temperature experimental data[36]. Recent experiments in shock tubes[37,38] cast doubt on the low-temperature results, although in themselves they are still insufficient for determination of the values of the quenching constant, because of the large experimental errors. Up to the present, only one attempt[39] has been made to calculate the constants k_1 and k_{-1} with allowance for all possible interactions responsible for the change in the electronic state of M.

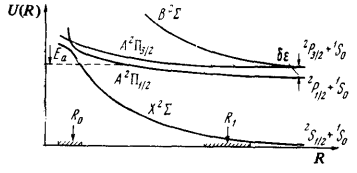


Figure 1. Lower adiabatic terms of the alkali metal atom–inert gas atom system.

As far as the adiabatic terms are concerned, non-empirical calculations have been carried out apparently only for the Li–He system[40,41], which gives the behaviour of the terms for the alkali metal–inert gas general case (Fig. 1). For heavy atoms X, however, the polarisation interaction may be so great that the activation energy E_a of process (1) will be equal to zero. Nevertheless, in order to be specific, we will consider the case for which the qualitative arrangement of the terms corresponds to the picture given in Fig. 1 ($E_a > 0$) and corresponding to a light inert gas.

The change in the electronic state of the colliding pair M and X takes place close to the internuclear distance R_0. In accordance with the usual classification, the ground electronic state of the combined system should be classified as $X^2\Sigma$. At R_0 this term is found to be close to the term of the first excited state $A^2\Pi_\Omega(\Omega = 1/2,\ 3/2)$, which has a fine structure. When $R \to \infty$, this term correlates with the atomic states $^2P_{1/2} + {}^2S$ and $^2P_{3/2} + {}^2S$. Rotation of the colliding pair mixes the states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, and this is usually described as a transition from Hund's coupling case a to coupling case b. Each of the two new states in turn is split into two components as a result of non-adiabatic coupling with the close $X^2\Sigma$ state (so called Λ-splitting). Finally, radial movement induces a non-adiabatic transition, since the coupling coefficients are markedly dependent on R. Mathematically, the problem reduces to the solution of three coupled equations for $A_\eta(t)$ within the framework of the linear model first examined by Landau[9] and Zener[10]. A more exact version of the theory[14] takes account of tunneling, which is important for high activation energy or for strong spin-orbital interaction. It has been found that in the semi-classical approximation the probability of a transition can be obtained by simple summation of the fluxes for each electronic term, calculated as if there were independent coupling between each pair of terms at their point of intersection[15]. This denotes the absence of interference between the probability amplitudes for the terms $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, although the phase difference between the two points of intersection is generally small.

Thus the theory gives extremely general expressions for k_1 and k_{-1}, leaving the theoretical parameters indeterminate. The rate constants can be estimated from familiar expressions[42] with the condition that there are some indications of the magnitude of the activation energy. On the other hand, if the temperature dependence of k_{-1} were measured sufficiently accurately, the theory would make it possible to interpret reaction (1) in terms of the adiabatic characteristics of the pair M and X. This has not yet been done. The only reliable conclusion is that the exchange of electronic and translational energy on atomic collisions has a low probability[43].

Let us now consider the deactivation of excited atoms by diatomic molecules. A number of experiments show that this deactivation takes place extremely effectively[44-48]. This suggests that in these processes there is resonance between an electronic level of the excited atom and the vibrational levels of the molecule. This problem has not been examined theoretically. Apart from the very difficult problem of solving the coupled wave equations (or the corresponding time-dependent equations of the semi-classical approximation), there arises another problem, associated with the possibility that the representative point passes repeatedly through the region where the adiabatic potential surfaces intersect or approach close to one another. Even if all the quantum-mechanical interference effects are neglected, it is very difficult to take account of all the contributions to the probability of a non-adiabatic transition from different points on the two-dimensional or multi-dimensional trajectory.

One of the simplest processes of this kind

$$Na^*(^2P) + N_2(^1\Sigma_g^+,\ v=0) \rightarrow Na(^2S) + N_2(^1\Sigma_g^+,\ v \geqslant 0) \qquad (2)$$

was examined by Bjerre and Nikitin[49], and also by Bauer[50]. These workers first tried to interpret it as a non-adiabatic transition between covalent adiabatic surfaces, produced from the energy states $^2P + {}^1\Sigma_g^+$ and $^2S + {}^1\Sigma_g^+$ of the separated interacting species. These surfaces for a fixed (N–N) distance are represented qualitatively in Fig. 2 in terms of relative coordinates R and Θ (the intermolecular distance and the angle of orientation). The Figure also shows the quantum numbers of the adiabatic states in the zeroth approximation for the symmetries $C_{\infty v}$, C_{2v}, and

C_s. With reasonable assumptions regarding the interactions, however, this attempt proved unsuccessful. Following Laidler[51,52] and Mori[53], the authors supplemented the system of covalent terms with an ionic term. In the zeroth approximation there then arise three potential surfaces: the purely covalent I $[Na(^2P) + N_2(^1\Sigma_g^+)]$, the purely ionic II $\{Na^+ + [N_2(^3\Sigma_u^+)]^-\}$, and the purely covalent III

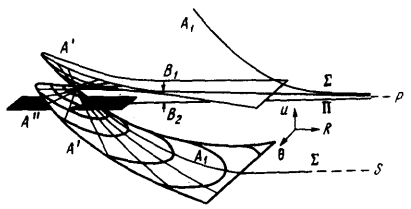


Figure 2. Lower adiabatic terms of the zeroth approximation (the spin-orbital coupling is not taken into account) for the alkali metal atom-nitrogen molecule system. The N–N distance is fixed, and the interaction with the ionic term is not taken into account.

$[Na^g(^2S) + N_2(^1\Sigma_g^+)]$. The ionic surface and the interaction matrix element $\delta V_{nn'}$, corresponding to non-adiabatic coupling between the adiabatic functions of the zeroth approximation, were calculated approximately[49] from experimental data[54] on the resonance scattering of slow electrons by N_2. The general arrangement of the surfaces for linear collision is shown in Fig. 3. Here R denotes the distance between the Na atom and the centre of the N_2 molecule, and r the interatomic distance in the N_2 molecule. The coordinates r_I, r_{II}, and r_{III} correspond to the equilibrium interatomic distances in the N_2 molecule in the corresponding

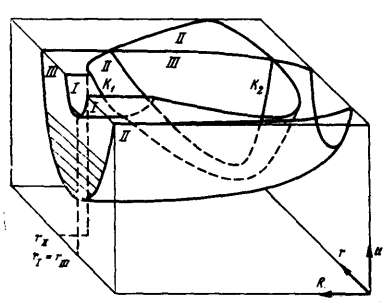


Figure 3. Lower adiabatic terms of the zeroth approximation (the interaction between the ionic term and the covalent terms is not taken into account) for the alkali metal atom-nitrogen molecule system. Linear arrangement of the atoms. Term I—excited covalent state; term II—ionic intermediate state; term III—covalent ground state.

electronic states for an infinitely large distance between the interacting pair ($R \to \infty$). The surfaces I–II and II–III intersect along the lines K_1 and K_2. If the non-diagonal elements of the interaction are taken into account, the intersections are converted into pseudo-intersections. When a certain trajectory L of the representative point reaches the lines K_1 or K_2, there is a certain probability of branching, leading to the appearance of two trajectories. The Landau–Zener formula was used to calculate the probability of the trajectory, and the trajectories were found by computer solution of the classical problem. Analysis of the trajectories made it possible to calculate the partial cross-sections and rate constants for reactions leading to a definite vibrational state v, and also led to the following general conclusions: (1) there is no indication that vibronic resonance is significant in process (2); (2) although the ionic surface shows a fairly deep minimum, the breakdown of $Na^+–N_2^-$ into $Na(^2S) + Na_2(^1\Sigma_g^+, v)$ takes place approximately in the time of one collision. This means that, for effective energy transfer, the formation of a long-lived intermediate complex is not essential, although it is possible that in other instances the formation of a complex facilitates the energy redistribution[55]; (3) the distribution with respect to vibrational levels is very sensitive to the magnitude of the splitting of the electronic terms of the zeroth approximation. Nevertheless, for process (2) a "reasonable" distribution function corresponding to the maximum at $v = 2$ and 3 was found. This conclusion shows qualitative agreement with experiment. An example of the calculated distribution function for the N_2 molecule with respect to the vibrational states is given in Fig. 4.

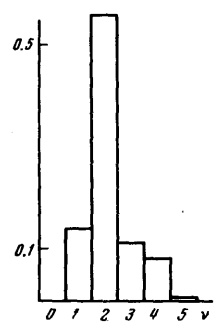


Figure 4. Example of the distribution function with respect to vibrational states for an N_2 molecule excited in the non-adiabatic process (2).

These non-adiabatic transitions take place between electronic terms with the same symmetry. The electronic transition is induced by the movement of the atoms in the plane (coordinates z and y from Table 4) and, to a much smaller extent, by rotation in the plane (R_x) and by spin-orbital interaction.

Another interesting example is provided by the reactions

$$Hg^*(^3P_0) + CO(^1\Sigma^+,\ v=0) \rightarrow Hg(^1S_0) + CO(^1\Sigma^+, v>0), \quad (3a)$$

$$Hg^*(^3P_0) + NO(^2\Pi,\ v=0) \rightarrow Hg(^1S_0) + NO(^2\Pi,\ v>0) \quad (3b)$$

of which the first is less effective than the second[46,47]. In the case of mercury the spin-orbital interaction is so great that it must be included in the electronic Hamiltonian. The initial state in process (3a), produced from $^3P_0 + {}^1\Sigma^+$, should then be classified as the one-dimensional representation A'' of the point group C_s of a system of three atoms. The final state $(^1S_0 + {}^1\Sigma^+)$ corresponds to the symmetry A',

since the transition (3a) is induced by rotation of the complete system by R_z or R_y. For process (3b) the initial and final states correspond to the same symmetry—both belong to the two-dimensional representation E''. This allows the movements in the plane (z and y) to be active in inducing transitions. These two mechanisms provide a qualitative explanation of the difference in the efficiencies of electronic deactivation on collisions with molecules having complete or incomplete electronic sublevels. We shall return to this problem below in connection with the transfer of vibrational energy.

5. TRANSFER OF SMALL AMOUNTS OF ELECTRONIC ENERGY

If an electronic transition takes place between two close energy states as a result of a collision, the cross-section for this process will be large. The probability of a transition depends on the magnitude of the minimal splitting between the adiabatic terms $\Delta\epsilon^{min}$, on the effective dimensions a of the region of the transition, and on the velocity of the nuclei in this range v. The parameter determining chiefly the magnitude of the probability of a transition is the ratio $\xi^{min} = \Delta\epsilon^{min}a/\hbar v$ (the so called Massey parameter), the probability of the transition being exponentially small for $\xi^{min} \gg 1$. Within the framework of the Landau-Zener model, applicable for electronic deactivation, $a \simeq \Delta\epsilon^{min}/\Delta\epsilon\alpha$, where $\Delta\epsilon$ is the energy of the reaction and α the orbital exponent of the outer electron. We thus obtain:

$$\xi^{min} \simeq \frac{(\Delta\varepsilon^{min})^2}{\hbar\alpha v\Delta\varepsilon} = \left(\frac{\Delta\varepsilon^{min}}{\Delta\varepsilon}\right)^2 \xi^{\infty},\ \xi^{\infty} = \frac{\Delta\varepsilon}{\hbar\alpha v}\ , \qquad (4)$$

the linear model being applicable only for the following conditions [35]

$$\xi^{\infty} \simeq \frac{\Delta\varepsilon}{\hbar\alpha v} \gg 1,\ \frac{\xi^{min}}{\xi^{\infty}} \simeq \frac{(\Delta\varepsilon^{min})^2}{\Delta\varepsilon^2} \ll 1\ . \qquad (5)$$

If in a non-adiabatic process one of the inequalities (5) is not fulfilled, the linear model should be replaced by a more general model.

An illustrative example is provided by the reactions

$$M^*(^2P_{1/2}) + X(^1S_0) \rightarrow M^*(^2P_{1/2}) + X(^1S_0) + \delta\varepsilon \qquad (6)$$

in which the collisions induce mixing of the components of the multiplet of the fine structure in the excited atoms of the alkali metal. These processes have been studied experimentally in fairly complete detail, and an extremely marked change in cross-sections was observed in the order M = Na, K, Rb, and Cs.[56] For all processes of this kind, we have $\xi^{\infty} \simeq \xi^{min}$ and under the conditions of the experiment the relationship $\xi^{min} \geq 1$ is satisfied. The mechanism of the change in quantum number is clear from Fig. 1. Mixing takes place at fairly large distances R_1 and, in accordance with Table 3, is brought about by radial movement and rotation, the former making the chief contribution. The theory based on non-linear models[57,58] predicts, in agreement with experiment, a variation in cross-section from the large value of 10^{-14} cm^2 for the Na*–He pair to the extremely small value 10^{-21} cm^2 for the Cs*–He pair. If we make the reasonable estimate $\Delta\epsilon^{min} \simeq \delta\epsilon$, it can be seen that

$$\xi^{min}_{quench} \simeq \left(\frac{\delta\varepsilon}{\Delta\varepsilon}\right)^2 \xi^{min}_{mix}\ . \qquad (7)$$

Thus even if intramultiplet transitions have a low probability ($\xi^{min}_{mixing} \gg 1$), electronic deactivation may be effective, since $\delta\epsilon/\Delta\epsilon \ll 1$. The true efficiency of deactivation of the excited state of course depends on the magnitude of the activation energy (see previous section).

If the inert gas atom is replaced by an inert diatomic molecule $X_2(^1\Sigma_g^+)$, we can expect an increase in the cross-section for the mixing of the components of the multiplet as a result of the contribution of the rotational and vibrational degrees of freedom to the overall process. Under these conditions, an increase in cross-section as a result of vibronic resonance is extremely probable, since resonance leads to a significant change in the selection rules for the vibronic spectrum relative to the selection rules in the independent electronic and vibrational spectra. A reaction of type (6) with replacement of X by X_2 is not very illustrative in this connection, since all the vibronic terms belong to the same two-dimensional representation E'', so that there are no special selection rules.

The following reactions provide a clearer example:

$$Hg^*(^3P_1) + Ar(^1S_0) \rightarrow Hg^*(^3P_0) + Ar(^1S_0) + \delta\varepsilon \qquad (8a)$$

$$Hg^*(^3P_1) + N_2(^1S_0) \rightarrow Hg^*(^3P_0) + N_2(^1\Sigma_g^+,\ v=1) + \delta\varepsilon - \hbar\omega\ . \qquad (8b)$$

The correlation diagrams for the adiabatic terms of the Hg*–Ar pair are given in the right-hand side of Fig. 5. It can be seen from Table 3 that process (8a) is due to rotational (R_x) mixing of the molecular states $\Omega = 0^-(^3P_0)$ and $\Omega = 1(^3P_1)$. The probability of the process is extremely small, since the Massey parameter is large (small exponential factor), and the terms have different symmetries (additional small pre-exponential factor). It is known from experiment that reaction (8a) proceeds very slowly[43]. On the other hand, reaction (8b) proceeds very rapidly, almost in every collision. This fact cannot be attributed simply to a decrease in the Massey parameter, in replacing $\delta\epsilon$ by $\delta\epsilon - \hbar\omega$. The true reason for the increase in efficiency can be seen from the correlation diagram.

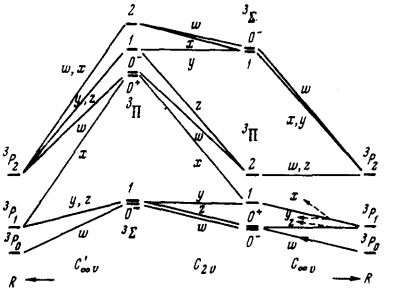


Figure 5. Correlation diagram of adiabatic terms of the system $^2P_j + {}^1S_0$ ($C_{\infty v}$ symmetry) and the system $^3P_j + {}^1\Sigma_g^+$ (C_{2v} and C_s symmetry). The symbols x, y, z, and w correspond to those of Table 4.

For system (8b) with a fixed vibrational quantum number, there are two relative displacements in the plane (z and y). We shall restrict ourselves to a discussion of a specially selected section of the system of two-dimensional adiabatic potentials, by following throughout a path in which the system retains the formal symmetry $C_{\infty v}$ and C_{2v}. Along this path we shall vary the three interaction parameters V_x, V_y, and V_z, which correspond to the three electronic states A_1, B_1, and B_2, produced from the spin-free P state. This section is determined as follows (from right to left in Fig. 5).

1. Free species:

$$V_x = 0,\ V_y = 0,\ V_z = 0.$$

2. $C_{\infty v}$ symmetry:

$$V_x = 0,\ V_y = 0,\ 0 < V_z < V_0.$$

3. C_{2v} symmetry:

$$V_x = 0,\ 0 < V_y < V_0,\ V_z = V_0\ .$$

4. $C_{\infty v}$ symmetry:

$$0 < V_x < V_0,\ V_y = V_0,\ V_z = V_0\ .$$

5. Free species displaced along the energy scale:

$$V_x = V_0,\ V_y = V_0,\ V_z = V_0\ .$$

The broken line shows the splitting of the levels, degenerate for $C_{\infty v}$ symmetry, if the section is defined in a slightly different way (stage 3 replaced by 3a). In this case we have the following situation.

3a. C_{2v} symmetry:

$$V_x = 0,\ 0 < V_y < V_0,\ 0 < V_z < V_0.$$

Decrease in symmetry from C_{2v} to C_S does not lead to further splitting—the only change is in the adiabatic mixing of the states of the same symmetry.

The arrangement of the vibronic terms for states with different quantum numbers v is obtained by superposition of diagrams of this kind with a displacement by $\hbar\omega$. This leads to intersection of the terms. Some of them are converted into pseudo-intersections, after the interaction δV is taken into account. Detailed study[59] shows that reaction (8b) induces combined movement along the coordinates z and y (radial and tangential relative movement of the interacting species), which mixes two states of symmetry A'', correlating with the states $^3P_1 + {}^1\Sigma_g^+$, $v = 0$, and $^3P_0 + {}^1\Sigma_g^+$, $v = 1$ of the interacting pair. The main contribution is made by the configuration close to the configuration of an isosceles triangle. For C_{2v} symmetry, these two states are classified as w (or A_2) and x (or B_2). These two terms have different symmetry and intersect the symmetric configuration; the two vibronic A'' states mentioned above refer to an adiabatic surface in the form of a double cone. It is this feature—the intersection of two terms with the same symmetry in a single point—which provides the fundamental difference between the atom–molecule process (8b) and the atom–atom process (8a). The rotation R_x also makes a contribution to the transition (8b), but its effect is relatively small, whereas for (8a) the rotation R_x is the only perturbation.

6. TRANSFER OF VIBRATIONAL ENERGY

In the previous sections it was shown that the removal of the degeneracy of the electronic state of one of the interacting species plays a large part in the mechanism of the exchange of electronic energy. By analogy, it may be expected that the transfer and exchange of vibrational energy will be different for interacting species with complete or incomplete electronic sublevels. This is in fact the case[60,61]. The physical picture is as follows. The intermolecular interaction leads to splitting (other than the Kramers doublet) of the degenerate electronic term of one of the interacting species, and at a certain distance this splitting becomes equal to the vibrational quantum. As a result of vibronic resonance, there is a high probability of energy exchange between the vibrational and translational movement.

Let us consider first the collision of a diatomic molecule with an inert gas atom, leading to the vibrational transition $v = 1 \rightarrow v = 0$. If the molecule is in a non-degenerate electronic state, both vibronic states correspond to symmetry A' (or A''). In accordance with Table 5, the transitions are then brought about by the perturbations z, y, and R_x. The first two represent relative movement and rotation, and their contribution depends on the corresponding reduced masses. Overall rotation in the plane does not make a significant contribution to the probability of the transition. If, however, the molecule is in, for example, a Π state, states of both types of symmetry A' and A'' are produced on interaction. With allowance for the spin-orbital interaction, the term $^2\Pi$ is split into components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, and the possible intersections of the terms $^2A'$ and $^2A''$ are converted into pseudo-intersections. The system of vibronic terms produced in this way is shown in Fig. 6. If the spin-orbital interaction between the vibronic states is small, it can be regarded[59] as the reason for the transition, together with the rotations R_y and R_z.

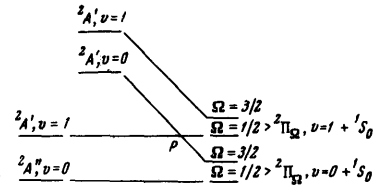


Figure 6. Correlation diagram of vibronic adiabatic terms of the system $^2\Pi_\Omega$; $v + {}^1S_0$ (or $^1\Sigma_g^+$).

Two possible paths of the vibrational transition in the above system are:

the adiabatic path

$$^2\Pi_{1/2}, v = 1 \rightarrow P \rightarrow {}^2A'', v = 1 \rightarrow {}^2A', v = 0 \rightarrow {}^2\Pi_{1/2}, v = 0, \quad (9)$$

the non-adiabatic path

$$^2\Pi_{1/2}, v = 1 \rightarrow P \rightarrow {}^2A'', v = 1 \rightarrow P \rightarrow {}^2\Pi_{1/2}, v = 0 \rightarrow {}^2\Pi_{1/2}, v = 0.$$

For two diatomic molecules, the arrangement of the vibronic states will be more complicated, but the general features are retained. As an illustration, we give here three reactions which have now been fairly well studied:

$$O_2(v = 1) + O_2(v = 0) \rightarrow O_2(v = 0) + O_2(v = 0) + \hbar\omega,\ O_2(^3\Sigma_g^-), \quad (10a)$$

$$NO(v = 1) + NO(v = 0) \rightarrow NO(v = 0) + NO(v = 0) + \hbar\omega,\ NO(^2\Pi_\Omega), \quad (10b)$$

$$N_2(v = 1) + N_2(v = 0) \rightarrow N_2(v = 0) + N_2(v = 0) + \hbar\omega,\ N_2(^1\Sigma_g^+), \quad (10c)$$

Of these processes, only reaction (10b) relates to interacting species with electronic terms quasi-degenerate in space. As a result of the interaction, the states of the system $NO(^2\Pi) + NO(^2\Pi)$ move apart as the interacting species approach. In the system $N_2(^1\Sigma_g^+) + N_2(^1\Sigma_g^+)$ splitting does not take place at all, and in the system $O_2(^3\Sigma_g^-) + O_2(^3\Sigma_g^-)$ electrostatic interaction cannot alter the fine structure of the spatially non-degenerate terms. Detailed examination shows that the main contribution to process (10b) is made as a result of spin-orbital interaction between the lower states $^1A'$ and $^3A''$, correlating with the states $^2\Pi + {}^2\Pi$ of the free species[60]. The Massey parameter for the adiabatic path, as for process (9), is greater than that for the non-adiabatic path, but the interaction is stronger for the adiabatic path (since states with the same symmetry

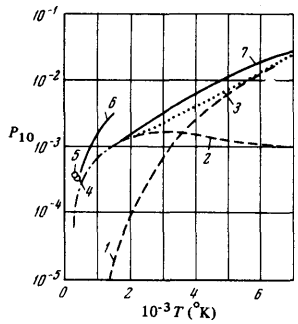


Figure 7. Adiabatic (*1*) and non-adiabatic (*2*) contributions to the total (*3*) probability P_{10} of the vibrational transition $v = 1 \rightarrow v = 0$ for the NO molecule. The points and curves *4–7* correspond to different experimental data[62].

are taking part). Thus these two paths compete, and at low temperature the non-adiabatic process predominates. Thus at room temperature the rates of processes (10a) and (10c) are smaller by three or four orders of magnitude than the rate of process (10b). This competition of the two mechanisms is shown in Fig. 7, taken from Wray's paper[62].

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