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Vibrational relaxation and vibrational predissociation as dynamic tunnelling processes

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Abstract. The dynamics of vibrational relaxation and vibrational predissociation processes, forbidden by the classical adiabatic Ehrenfest principle, are examined. A general approach to the calculation of rate constants for processes represented by total collision and half-collision models is formulated. Simple models which make it possible to understand the characteristics of the processes discussed are described and are extended to the case of real three-dimensional motion. Examples providing a fairly complete illustration of the present understanding of dynamic tunnelling processes are presented. The bibliography includes 45 references.

I. Introduction

The vibrational relaxation of molecules in gases is an energy exchange process between the vibrational degrees of freedom of a molecule and the translational and rotational degrees of freedom as a result of collisions between molecules and the particles of a heat reservoir. The mechanism of this process is especially simple in the case of diatomic molecules where there is only one vibrational degree of freedom and there is no intramolecular energy exchange in the intervals between successive collisions.

The experimental studies of energy transfer processes involving diatomic molecules have been some of the first investigations which laid the foundations for a new field in chemistry—chemical physics (see, for example, Kondrat'ev[1]). At the present time, these processes continue to be investigated vigorously by methods which permit the measurements not only of thermal rate constants for transitions between specified vibrational states of the molecules $n \to n'$ but of also the state-to-state rate constants for transitions between specific vibrational and rotational states: $n, j \to n', j'$.

We shall confine ourselves to the discussion of the mechanisms of purely vibrational transitions and methods for the calculation of the rate constants $k_{nn'}(T)$. We shall begin with the fact that the distribution of energy among rotational and translational degrees of freedom is canonical, i.e. is described by a Boltzmann distribution with a temperature T. We shall also assume that the heat reservoir consists of a monatomic inert gas A. The elementary collision step

$$A + BC(n) \to A + BC(n'), \qquad (1)$$

as a result of which the vibrational energy of the molecule changes by an amount $\Delta E_{nn'} = E_{n'} - E_n$, is thus discussed. The energy $\Delta E_{nn'}$ is either converted into the energy of the translational motion of A and BC and into the rotational energy of BC in the case of a deactivating collision ($\Delta E_{nn'} < 0$) or is borrowed from these degrees of freedom in the case of an activating collision ($\Delta E_{nn'} > 0$). We shall designate the rate constant for process (1) by $k^{\mathrm{rel}}_{nn'}(T)$.

Together with vibrational relaxation processes, the processes involving the so-called vibrational predissociation of weakly bound (usually van der Waals) complexes are widely investigated nowadays:

$$A \cdots BC(n) \to A + BC(n'). \qquad (2)$$

In process (2), a weak bond between the atom A and the molecule BC is ruptured as a result of the conversion of part of the vibrational energy of the molecule BC into the energy of the relative motions of A and BC. We shall designate the rate constant for process (2) by $k^{\mathrm{diss}}_{nn'}(T)$.

Clearly the mechanisms of processes (1) and (2) have much in common. In recognition of this fact, a terminology has been established in modern literature according to which process (1) is referred to as a total collision and process (2) as a half-collision.

We shall consider below the mechanisms of the total collision (1) and the half-collision (2) from a single standpoint within the framework of the so-called method of optimum trajectories. In this method, the dynamics of the collision is characterised by a single trajectory, which describes the relative motion of A and BC and the rotation of BC. The possibility of operating with one trajectory and not with a large set of trajectories, normally employed in the theoretical study of the dynamics of molecular processes,[2-4] is associated with the specific features of the vibrational relaxation and predissociation: processes of both types are forbidden in classical terms. At the same time, the optimum trajectory is not a fully classical object because it requires the introduction of the concept of the evolution of a classical system during an imaginary time interval.

Henceforth we shall consider for simplicity two limiting cases where the molecule BC is homonuclear (or 'almost' homo-

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nuclear) or where it is highly asymmetric (for example, the molecule of a hydrogen halide). The preferred VT (vibrational–translational) or RT (rotational–translational) mechanisms can be isolated in this way from the overall mechanism of the so-called VRT process (vibrational–rotational–translational energy exchange). It is found that the vast majority of molecules can be assigned, from the standpoint of the energy exchange mechanism, to one of these groups. The present article does not claim to represent a complete survey of the theoretical questions associated with relaxation and predissociation processes to which a very extensive literature is devoted nowadays. Thus the interpretation of the existing experimental results within the framework of the models described above has been described in recent reviews.[5,6]

This review is constructed as follows. First the characteristic features of the dynamics of processes forbidden by the classical adiabatic Ehrenfest principle are discussed. Next we formulate a general approach to the calculation of the rate constants for processes which represent the total collision and the half-collision, and simple models which make it possible to understand the characteristics of the processes discussed are described and also extended to real three-dimensional collisions. The review ends with examples which illustrate fairly completely the present understanding of the dynamic tunnelling processes.

II. Vibrational relaxation and vibrational predissociation as classically forbidden processes

The transitions between the vibrational levels n and n' of a molecule BC in the region of thermal energies are as a rule forbidden in classical terms. This means that the solution of the classical problem of the vibrational activation or deactivation in process (1) leads to the following result: none of the multidimensional trajectories, beginning at an arbitrary point in the phase space corresponding to the classical vibrational state $N = \hbar(n + \frac{1}{2})$, ever reaches a point in the phase space which would correspond to the final vibrational state $N' = \hbar(n' + \frac{1}{2})$. For process (2), this fact means that any trajectory which describes in the initial state the complex with the vibrational energy corresponding to the classical state $N = \hbar(n + \frac{1}{2})$ in the final state describes dissociation products in which the change in the vibrational energy of BC is less than a single vibrational quantum.

The classical unattainability of the final state n' shows that processes (1) and (2) are in a certain sense tunnel processes. However, this type of tunnelling, referred to in the literature as dynamic tunnelling, differs significantly from the familiar tunnelling through a potential barrier.[7–9] Tunnelling through a potential barrier has no classical analogy, whereas the energy exchange in process (1) and the dissociation in process (2) do have classical analogies. However, these analogies do not permit the determination by the usual quasi-classical method of the probability of the transition from a solution of the classical problem, as was done, for example, within the framework of the classical S-matrix method based on the correspondence principle.[10,11]

At the same time, the classical prohibition of the $n \to n'$ transitions means that the quantum probability of processes (1) and (2) is low and it is therefore possible to employ a particular version of the perturbation theory for its calculation. In principle, this is indeed so. However, the application of this approach in practice is extremely complex, since the wave functions of the initial and final states, taking into account the strong interaction between the relative translational motions A–BC and the rotation of BC are not known with adequate accuracy. In other words, before solving the problem of the vibrational transition, one must solve fully the problem of the energy exchange between the translational and rotational degrees of freeedom at the level of the determination of the wave functions of the rotational inelastic scattering (and not only at the level of the calculation of the probabilities of the translational–rotational transitions which are determined solely by the asymptotic behaviour of the scattering wave functions).

Since the relative motions of A and BC and the rotation of BC under typical conditions satisfy the quasi-classical conditions, it is desirable to formulate a method which would operate with classical trajectories describing the motion in terms of these degrees of freedom. However, the following difficulty arises in this instance. If the classical description is adopted, then, for a very small change δN in the classical initial vibrational action N, the projection of the total exact multidimensional trajectory (for a vibrational non-elastic process) onto the translational–rotational subspace is located very close to the vibrational-elastic trajectory. In a quantum description, the minimum change in the quantum number $\delta n = n' - n$ cannot be less than unity and the corresponding change in the classical action $\delta n \times \hbar$ cannot therefore exceed δN. Under such conditions, the significance of the unperturbed trajectory becomes obscure even when the probability of the transition is very low. One of the possible ways of retaining the classical description of motion in terms of translational and rotational degrees of freedom is provided by the method of optimum trajectories (OT) which is described briefly below. This method has been applied to the description of the dynamics of the vibrational relaxation of molecules in a solid matrix, non-radiative transitions in molecules, and the photodissociation of molecules in a number of studies.[12–14]

For a specified vibrational transition $n \to n'$, the OT method defines the 'classical' trajectory of the translational–rotational motion (i.e. the pathway which satisfies the classical equations of motion) along which the system evolves during a complex time interval; this trajectory need not necessarily be either continuous or real. When the trajectory has been found, the probability of the transition is determined within the framework of perturbation theory. An important property of the OT method is the possibility of a comparatively simple averaging over the initial canonical distribution, since the quantum operator of the evolution and the operator of the Boltzmann distribution have the same (exponential) form. In calculations on the system dynamics, the canonical averaging is carried out with a displacement along the time axis by the imaginary increment $i\hbar/kT$.

The OT method is one of the versions of the so-called semiclassical methods based on the subdivision of all the degrees of freedom of the system under consideration in two subsystems —quantum and classical. The interaction between these subsystems is described within the framework of the non-stationary quantum perturbation theory. The simplifications arising in this instance are evident. Instead of a general consideration of the quantum problem for the entire system, an approach in stages is proposed: one solves initially the dynamic problem only for the classical subsystem, after which the simplified dynamic problem is solved for the quantum subsystem. However, the non-trivial question of the adjustment for self-consistency of the motions of the above two subsystems arises under these conditions. The OT method, discussed below, makes possible such adjustment for consistency.

The idea of the OT method in relation to the calculation of the rate constants for processes (1) and (2) will now be expressed in concrete terms. Other methods for the description of vibrational energy transfer processes have been described in books and reviews.[15–17]

III. Correlation functions for the interaction and the rate constants for relaxation and predissociation

We shall begin the consideration of the computational methods for the first-order time-dependent perturbation theory having assumed that the relative motion of A and BC and the rotation of BC are described in classical terms, while the BC vibrations are described in terms of quantum mechanics. We shall call this approximation semiclassical (SC). The potential energy surface for the system considered depends on three coordinates— the

distance R between the atom A and the centre of gravity of the molecule BC, the distance r between the atoms B and C, and the angle γ between the vectors $\boldsymbol{R}$ and $\boldsymbol{r}$. Instead of the variable r, it is frequently convenient to use another variable $x = r - r_e$, i.e. the deviation of the distance r from its equilibrium value r_e in a free molecule BC.

In the zeroth approximation, we have a five-dimensional trajectory $\boldsymbol{Q}(t)$ which describes the rotational non-elastic collision of A with BC for a fixed vibrational quantum number of BC ($\boldsymbol{Q}$ designates the set of coordinates which specify the relative positions of A and BC in space—three coordinates for translational motion and two coordinates for rotational motion). If $V_{nn'}(\boldsymbol{Q})$ is a matrix element of the interaction which relates the vibrational states n and n', then the probability of the first-order transition is

$$P_{nn'}^{\mathrm{SC}} = \left| \int V_{nn'}[\boldsymbol{Q}(t); \boldsymbol{Q}_i, \boldsymbol{P}_i] \exp(\mathrm{i}\omega_{nn'}t) \frac{\mathrm{d}t}{\hbar} \right|^2 , \tag{3}$$

where the time integral is with respect to the classical five-dimensional trajectory. Here account has been taken explicitly of the fact that the probability $P_{nn'}^{\mathrm{SC}}$ depends on the coordinates $\boldsymbol{Q}_i$ and the momenta $\boldsymbol{P}_i$ of the system before the collision. Eqn. (3) shows that the probability of the transition is proportional to the square of the Fourier component of the matrix element of the interaction energy at the vibrational transition frequency. The rate constant is determined from the probability of the transition by integrating it with respect to the initial collision parameters.

A more convenient representation is obtained after a series of transformations, which express the rate constant for the transition simply as the Fourier component of a bilinear combination of the matrix elements of the interaction at the vibrational transition frequency, i.e. the following relations are valid:

$$k_{nn'}^{\mathrm{SC}}(T) = [F(\beta)]^{-1} W_{nn'}^{\mathrm{SC}}(T) , \tag{4}$$

where F is the partition function for the system in the initial state and $\beta = 1/kT$;

$$W_{nn'}^{\mathrm{SC}}(T) = \int_{-\infty}^{\infty} G_{nn'}^{\mathrm{SC}}(T, t) \exp(\mathrm{i}\omega_{nn'}t)\mathrm{d}t , \tag{5}$$

where $G_{nn'}^{\mathrm{SC}}(T, t)$ is the classical autocorrelation function of the matrix element of the interaction:

$$G_{nn'}^{\mathrm{SC}}(T, t) = \int \mathrm{d}\Gamma_0 (2\pi\hbar)^{-s} \exp[-\beta H(\boldsymbol{P}_0, \boldsymbol{Q}_0)] \times \\ \times V_{nn'}\left[\boldsymbol{Q}\left(\frac{t}{2}\right); \boldsymbol{Q}_0, \boldsymbol{P}_0\right] V_{n'n}\left[\boldsymbol{Q}\left(-\frac{t}{2}\right); \boldsymbol{Q}_0, \boldsymbol{P}_0\right] , \tag{6}$$

where $H(\boldsymbol{P}_0, \boldsymbol{Q}_0)$ is the hamiltonian of the A–BC system (excluding the vibrations of BC), which contains the potential energy $U(R, \gamma)$ for the interaction between A and the molecule BC corresponding to the equilibrium internuclear distance. In Eqn. (6), the integration with respect to the phase space of $\mathrm{d}\Gamma_0 = \mathrm{d}^s\boldsymbol{Q}_0\,\mathrm{d}^s\boldsymbol{P}_0$ is extended over the entire phase volume of the reactants (s is the number of degrees of freedom; in our case $s = 5$).

Evidently the translational and rotational degrees of freedom enter symmetrically into Eqn. (6), so that the latter is applicable to the calculation of both $k_{nn'}^{\mathrm{rel}}(T)$ and $k_{nn'}^{\mathrm{diss}}(T)$. In the former case, H represents the hamiltonian of the translational–rotational motion of the collision partners and F designates the products of the translational and rotational partition functions; the corresponding dimensions of $k_{nn'}^{\mathrm{rel}}(T)$ are $\mathrm{s}^{-1}\ \mathrm{cm}^{-3}$. In the second case, H is the hamiltonian of the van der Waals complex and F is the partition function of the complex taking into account its rotation as a whole and the hindered rotation of BC in the complex; $k_{nn'}^{\mathrm{diss}}(T)$ is expressed in s^{-1}.

If the transition $n \to n'$ is forbidden in classical terms, then the rate constant is exponentially small. This means that the overall expression for $k_{nn'}^{\mathrm{SC}}$ (here $k_{nn'}^{\mathrm{SC}}$ denotes both $k_{nn'}^{\mathrm{rel}}$ and $k_{nn'}^{\mathrm{diss}}$ calculated in terms of the semiclassical approximation) assumes the form

$$k_{nn'}^{\mathrm{SC}} = \Phi_{nn'}^{\mathrm{SC}} \exp(-\Psi_{nn'}^{\mathrm{SC}}) , \tag{7}$$

where $\Phi_{nn'}^{\mathrm{SC}}$ is the pre-exponential factor and $\Psi_{nn'}^{\mathrm{SC}}$ is a function which greatly exceeds unity in absolute magnitude and increases with increase in the energy transferred; it depends on the parameters of the interaction potential and temperature. The pre-exponential factor $\Phi_{nn'}^{\mathrm{SC}}$ also depends on these parameters but to a much lesser extent than the exponential part of Eqn. (7). From the symmetry of the probability of the transition, it follows that $\Phi_{nn'}^{\mathrm{SC}} = \Phi_{n'n}^{\mathrm{SC}}$ and $\Psi_{nn'}^{\mathrm{SC}} = \Psi_{n'n}^{\mathrm{SC}}$.

It is seen from Eqn. (7) that the rate constants for the forward ($n \to n'$) and reverse ($n' \to n$) processes are the same, i.e. $k_{nn'}^{\mathrm{SC}}(T)/k_{n'n}^{\mathrm{SC}}(T) = 1$, which conflicts with the principle of detailed balance:

$$\frac{k_{nn'}(T)}{k_{n'n}(T)} = \exp(-\beta E_{n'} + \beta E_n) . \tag{9}$$

Thus the semiclassical approximation is valid subject to the condition that the energy transferred $E_{n'} - E_n$ is small compared with kT, i.e. when the right-hand side of Eqn. (9) is close to unity. This condition does not usually hold for vibrational relaxation at not unduly high temperatures; it is even less likely to hold for vibrational predissociation when the temperature of the van der Waals complex is very low.

The semiclassical approximation (SC) can be refined by going over to the quasiclassical approximation (QC). The latter can also be used in our approach, since the quasiclassical wave functions can be constructed on the basis of an assembly of classical trajectories.[19] The required refinement is achieved by replacing the classical autocorrelation function by its quasi-classical analogue. The corresponding expression for G^{QC} is

$$G_{nn'}^{\mathrm{QC}}(T, t) = \int \mathrm{d}^s\boldsymbol{Q}' \int \mathrm{d}^s\boldsymbol{Q}'' \{V_{nn'}(\boldsymbol{Q}') V_{n'n}(\boldsymbol{Q}'') B(\boldsymbol{Q}', \boldsymbol{Q}'') \times \\ \times \exp[\mathrm{i}A_t(\boldsymbol{Q}', \boldsymbol{Q}'') - \mathrm{i}A_{t+\mathrm{i}\beta}(\boldsymbol{Q}', \boldsymbol{Q}'')]\} , \tag{10}$$

where A_t represents the classical action along the rotational–translational trajectory from the space–time point $-t/2$, $\boldsymbol{Q}'$ to the space–time point $t/2$, $\boldsymbol{Q}''$, while $A_{t+\mathrm{i}\beta}$ represents the action along another trajectory, which begins at the point $(t + \mathrm{i}\beta)/2$, $\boldsymbol{Q}'$ and terminates at the point $(t + \mathrm{i}\beta)/2$, $\boldsymbol{Q}''$. The complex quantity added to time ensures the canonical averaging of the transition probability. The multiplier B is expressed in terms of the determinants of the second-derivative matrices:

$$B(\boldsymbol{Q}', \boldsymbol{Q}'') = (2\pi\hbar)^{-s} \mathrm{Det}\left[\frac{\partial^2 A_t}{\partial Q_m \partial Q_k}\right] \mathrm{Det}\left[\frac{\partial^2 A_{t+\mathrm{i}\beta}}{\partial Q_m \partial Q_k}\right] . \tag{11}$$

Thus Eqns. (4) and (5) are replaced by

$$k_{nn'}^{\mathrm{QC}}(T) = F(\beta)^{-1} W_{nn'}^{\mathrm{QC}}(T) , \tag{12}$$

$$W_{nn'}^{\mathrm{QC}}(T) = \int_{-\infty}^{\infty} G_{nn'}^{\mathrm{QC}}(T, t) \exp(\mathrm{i}\omega_{nn'}t)\mathrm{d}t . \tag{13}$$

It follows from Eqns. (12) and (13) that

$$k_{nn'}^{\mathrm{QC}} = \Phi_{nn'}^{\mathrm{QC}} \exp(-\Psi_{nn'}^{\mathrm{QC}}) , \tag{14}$$

where $\Phi_{nn'}^{\mathrm{QC}} \gg 1$, but now $\Phi_{nn'}^{\mathrm{QC}} \neq \Phi_{n'n}^{\mathrm{QC}}$, and $\Psi_{nn'}^{\mathrm{QC}} \neq \Psi_{n'n}^{\mathrm{QC}}$. It can also be shown that the rate constants for the forward and reverse processes satisfy the principle of detailed balance:

$$\frac{k_{nn'}^{\mathrm{QC}}(T)}{k_{n'n}^{\mathrm{QC}}(T)} = \exp(-\beta E_{n'} + \beta E_n) . \tag{15}$$

The calculation of the integral (10) requires the preliminary determination of a large number of trajectories describing the rotational non-elastic processes and subsequent integration with respect to the initial and final states, i.e. the problem of the calculation of the rate constant still remains extremely complex. However, under certain conditions it can be simplified: instead of a large number of trajectories one seeks one trajectory [it is called henceforth the optimum trajectory (OT)] and the probability flux is determined within a comparatively narrow flux tube along the OT. All the properties of this flux are determined by the properties of the OT and also by the additional characteristics of the motion along the optimum trajectory, which are contained in the so-called monodromic matrix.

From the mathematical point of view, the OT method is in fact a generalisation of the stationary phase method for the calculation of quasi-classical matrix elements. Within the famework of this approximation, the optimum trajectory $\mathscr{L}^*$ is sought. It consists of two branches ($\mathscr{L}_i^*$ and $\mathscr{L}_{i+i\beta}^*$), each of which corresponds to the boundary conditions ($-t^*/2$, $\boldsymbol{Q}'^*$; $t^*/2$, $\boldsymbol{Q}''^*$) and ($-t^*/2-i\beta/2$, $\boldsymbol{Q}'^*$; $t^*/2 + i\beta/2$, $\boldsymbol{Q}''^*$) respectively. These conditions ensure a stationary value of the exponent in the exponential function. Next the difference between the actions $A_t - A_{t+i\beta}$ together with the product $V_{nn'}(\boldsymbol{Q}')V_{n'n}(\boldsymbol{Q}'')$ is expanded in series in the vicinity of this trajectory up to second-order terms in the deviations $\delta t = t - t^*$, $\delta\boldsymbol{Q}' = \boldsymbol{Q}' - \boldsymbol{Q}'^*$, and $\delta\boldsymbol{Q}'' = \boldsymbol{Q}'' - \boldsymbol{Q}''^*$, after which the integral with respect to δt, $\delta\boldsymbol{Q}'$, and $\delta\boldsymbol{Q}''$ is calculated.

We obtain as a result the following expression for k:

$$k_{nn'}^{\mathrm{OT}} = \Phi_{nn'}^{\mathrm{OT}} \exp(-\Psi_{nn'}^{\mathrm{OT}}) . \tag{16}$$

It can be shown that it satisfies the detailed balance relation. This expression will be used subsequently to elucidate the dependence of the rate constants on the principal parameters of the interaction between the species involved and temperarture.

IV. Models with a reduced dimensionality for VT and VR processes

In modern molecular dynamics calculations, the so-called models with a reduced dimensionality play a major role. The number of degrees of freedom in these models is reduced to a minimum set for which it is possible to reproduce the principal features of the process considered. The success of such models depends on how simply they can be extended to real cases. We shall describe below two such models: colinear collision of a species A with a harmonic oscillator BC (a model of a VT process) and interaction of a harmonic oscillator BC with a species A, perturbing the rotation of a planar rotator BC (a model of a VR process).

1. Model of a VT Process

The model involving the linear collision of a harmonic oscillator with a structureless species for the description of the vibrational and translational energies was examined by Landau and Teller[20] in 1936. Despite the enormous progress in the description of the dynamics of molecular collisions during the last decade by virtue of the use of computers, this model continues to be of interest because its principal predictions concerning the dependence of the probability of the transition on temperature and the interaction parameters remain in force for a wide range of interactions.

Since the Landau–Teller model is very simple, we shall use it to explain the principal ideas of the OT method and to derive two main relations, referred to in the literature as the law of the energy and momentum gaps. Next we shall supplement the Landau–Teller model by the principal correction for anharmonicity, which is important for the consideration of transitions between not unduly low vibrational states.

We shall consider the colinear collision of a diatomic molecule BC, modelled by a harmonic oscillator with a frequency ω, and a structureless species A (A–BC configuration), which interacts with the species B via an exponential repulsion potential $\exp(-\alpha R_{\mathrm{AB}})$. It is assumed that the vibrational amplitude x is small compared with $1/\alpha$, so that the product αx can be regarded as a small parameter of the perturbation theory.

Within the famework of the semiclassical approximation, one considers initially the motion of a classical subsystem (relative motion), which is described by the simple hamiltonian

$$H_{c1} = \frac{P^2}{2\mu} + A\exp(-\alpha R) , \tag{17}$$

where P is the momentum coupled with R, and μ is the reduced mass of the species involved—A and BC. The transitions in the quantum subsystem (vibrations) are induced by a time-dependent perturbation of the type

$$V(x,t) = \lambda\alpha x A \exp[-\alpha R(t)] , \tag{18}$$

where $\lambda = M_{\mathrm{C}}/(M_{\mathrm{C}} + M_{\mathrm{B}})$, M_{C} and M_{B} being the masses of the atoms C and B respectively. The trajectory $R(t)$ can be found from classical equations of motion by using the hamiltonian (17).

We shall consider initially the probability of the transition $n = 1 \to n' = 0$ averaged with respect to the thermal distribution of the collision energies. Knowing the analytical expression for $\langle P_{10}^{\mathrm{SC}} \rangle$ (see, for example, Nikitin[15]), we obtain the principal corrections to the semiclassical approximation within the framework of the OT method. The application of the stationary phase approximation to the integral (10) makes it possible to determine the points R'^*, R''^*, the optimum kinetic energy in the initial vibrational state E_{t1}^*, and the energy difference $E_{t1}^* - E_{t0}^* = \hbar\omega$. Instead of integrating with respect to the coordinates and time, it is possible to integrate with respect to the coordinates and the energy. The latter is equivalent to the calculation of the matrix element by the Landau method[20] with subsequent canonical averaging of the square of the matrix element. Omitting the intermediate steps, we shall only note that we are seeking a stationary value of the function

$$\begin{aligned}\Psi_{10}(R', R'', E_{t1}) = \alpha R' - \frac{\mathrm{i}}{\hbar}\int_{R_1}^{R'} P(R, E_{t1})\mathrm{d}R + \\ + \frac{\mathrm{i}}{\hbar}\int_{R_0}^{R'} P(R, E_{t0})\mathrm{d}R + \alpha R'' - \frac{\mathrm{i}}{\hbar}\int_{R_1}^{R''} P(R, E_{t1})\mathrm{d}R + \\ + \frac{\mathrm{i}}{\hbar}\int_{R_0}^{R''} P(R, E_{t0})\mathrm{d}R + \beta E_{t1} ,\end{aligned} \tag{19}$$

where R_1 and R_0 are the turning points in classical motion for the translational energies E_{t1} and $E_{t0} = E_{t1} + \hbar\omega$, and the momentum of the relative motion is given by the expression

$$P(R, E_t) = \{2\mu[E_t - A\exp(-\alpha R)]\}^{1/2} . \tag{20}$$

The first three terms in Eqn. (19) arise from the exponent of the first quasiclassical matrix element and the next three terms arise from the exponent of the second element (this yields the square of the matrix element), while the last term arises from the Boltzmann exponential function. The stationary conditions assume the form

$$\left.\begin{aligned} R'^* = R''^* &= R^* , \\ P(R^*, E_{t1}^*) - P(R^*, E_{t0}^*) &= \mathrm{i}\alpha\hbar , \\ t(R^*, E_{t1}^*) - t(R^*, E_{t0}^*) &= \mathrm{i}\beta\hbar , \end{aligned}\right\} \tag{21}$$

where $E_{t0}^* = E_{t1}^* + \hbar\omega$, and $t(R, E_{tk})$ is the classical time required for movement from point R_k to point R:

$$t(R, E_{tk}) = \int_{R_k}^{R} \frac{\mathrm{d}R}{v(R, E_{tk})} .$$

The first Eqn. (21) means that the stationary coordinate points coincide and define the 'transition distance' R^*. The second equation defines the change in momentum between the two parts

of the trajectory at the transition point. The third equation defines the difference between the times required to reach the transition point from the turning points. Hence the optimum energies E^*_{t0} and E^*_{t1} and the optimum turning points R^*_1 and R^*_2 are defined. For the case under consideration, R^* is a real quantity, while the momenta and the time are imaginary quantities. Fig. 1 illustrates the positions of these times in the phase space generated by the real variable R and the complex variable P as well as the two parts of the optimum trajectory (non-elastic transition) and the elastic transition trajectories *00* and *11*.

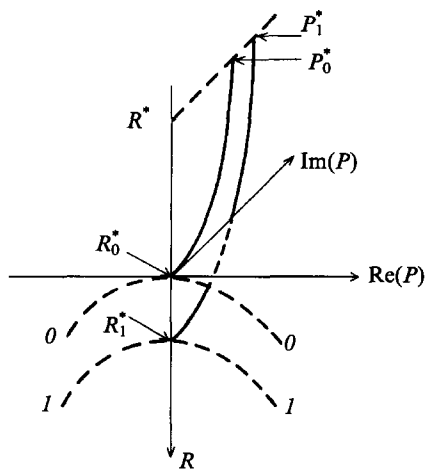


Figure 1. Optimum trajectory for vibrational relaxation in a linear A + BC ($n' = 0$) collision in the 'real coordinate–complex momentum' phase space. R^*_1 and R^*_0 are the turning points for the elastic scattering trajectories in the vibrational states with $n = 1$ and $n = 0$, while R^* is the non-elastic transition point.

In the language of classical trajectories, the vibrational deactivation in process (1) is described as follows. Initially the species approach one another along trajectory *1* from the left and reach the turning point R^*_1; they then 'penetrate' into the classically forbidden region, moving along the complex trajectory $R^*_1 - P^*_1$. At the point P^*_1, there is a sudden change in momentum (from P^*_1 to P^*_0) and the system returns to the turning point R^*_0 at which it 'emerges' from the classical forbidden region. From this point, the particles diverge to the right along the classically allowed trajectory *0*.

The function Ψ^{OT}_{10}, which defines the transition surface, is calculated in terms of R^* and E^*_{t1}, which are found from the second and third Eqns (21) and from the conditions for the conservation of energy, $E_{t0} = E_{t1} + \hbar\omega$:

$$\Psi^{OT}_{10} = \Psi_{10}(R^*, E^*_{t1}). \tag{22}$$

In an explicit form, we have

$$\Psi^{OT}_{10} = \frac{2\pi}{\hbar\alpha}\{[2\mu(E^*_{t1} + \hbar\omega)]^{1/2} - [2\mu E^*_{t1}]^{1/2}\} + \beta E^*_{t1}, \tag{23}$$

where E^*_{t1} is found from the equation

$$\frac{d\Psi^{OT}_{10}(E^*_{t1})}{dE^*_{t1}} = 0. \tag{24}$$

Henceforth we shall be interested in two limits corresponding to high and low temperatures.

In the high-temperature limit, when $\hbar\omega/E^*_{t1} < 1$, the expression for Ψ^{OT}_{10} can be written in the form

$$\Psi^{OT}_{10} \simeq \Psi^{SC}_{10} + \Delta\Psi^{OT}_{10}, \tag{25}$$

where $\Delta\Psi^{OT}_{10} = -\hbar\omega/2kT$ represents a relatively small correction to Ψ^{SC}_{10}:

$$\Psi^{SC}_{10} = 2\frac{\pi\omega}{\alpha v^*} + \beta E^* = 3\left(\frac{\theta^*}{T}\right)^{1/3}, \tag{26}$$

where $v^* = (E^*/2\mu)^{1/2}$ is the optimum relative rate of collision and $\theta^* = \pi^2\mu\omega^2/2\alpha k$ is the characteristic temperature of the model.

In the low temperature limit, when $\hbar\omega/E^* \gg 1$, Eqn. (23) becomes

$$\Psi^{OT}_{10} \simeq \Psi^{(0)}_{10} = \frac{2\pi}{\hbar\alpha}[2\mu\hbar\omega]^{1/2}, \tag{27}$$

where $\Psi^{(0)}_{10}$ denotes Ψ^{OT}_{10} at $T = 0$.

It follows from Eqn. (25) that in the high-temperature limit the exponent for the probability of the transition is proportional to the transferred energy $\hbar\omega$. This relation is called the energy gap law. The high-temperature limit is interesting in connection with vibrational relaxation processes. We may note that the Planck constant does not enter into the expression for Ψ^{SC}_{10}, which makes it possible to attribute the classical significance to this quantity. The correction $\Delta\Psi^{OT}_{10}$ characterises the difference between the quasiclassical and semiclassical descriptions.

In the low-temperature limit, the exponent is proportional to the transferred momentum $(2\mu\hbar\omega)^{1/2}$. This relation is called the momentum gap law. The low-temperature limit is interesting in connection with vibrational predissociation processes.

The application of the Landau–Teller model to predissociation processes requires additional comments. The repulsive potential in the Landau–Teller model cannot of course be used in the literal form for the description of the transition from the bound to the dissociated state. However, it is seen from Eqn. (23) that the probability of the transition between the states of the continuous spectrum is determined mainly by the momentum of the final state subject to the condition that it is appreciably greater than the momentum of the initial state. This factor permits the application of Eqn. (27) also to transitions between the bound state and the state corresponding to the continuous spectrum of the potential with a minimum (subject to the condition that the final energy exceeds appreciably the depth of the potential well: $\hbar\omega \gg \varepsilon$). It is also seen that the parameter α in Eqn. (27) should be interpreted as the logarithmic derivative of the potential at the turning point relative to the motion in the final state.

We shall now consider the general case of the transition $n \to n-1$ ($n \geqslant 1$) and at the same time we introduce the most important corrections for the anharmonicity of the vibrations. Clearly the latter arise solely due to the marked dependence of the exponent on the vibration frequency (which in the case of an anharmonic oscillator depends on its energy, i.e. on the number of the level). A linear dependence of the transition frequency ω_n on n is usually employed:

$$\omega_n = \omega(1 - 2x_e n), \tag{28}$$

where x_e is the anharmonicity parameter ($x_e \ll 1$). If the factor $\Phi^{SC}_{nn'}$ is calculated in terms of the harmonic approximation and account is taken of the linear (in terms of n) correction for anharmonicity in the exponent $\Psi^{SC}_{nn'}$, then the overall expression for the probability of the vibrational transition or vibrational predissociation can be written in the form

$$P^{r,d}_{n,n-1} = n\exp(\gamma^{r,d}n)P^{r,d}_{10}, \tag{29}$$

where $P^{r,d}_{10}$ are the probabilities of relaxation and predissociation for the transition $1 \to 0$ and the parameters $\gamma^{r,d}$ have a different significance for vibrational relaxation and vibrational predissociation:

$$\gamma^r = \Psi^{SC}_{10}x_e; \quad \gamma^d = \Psi^{(0)}_{10}x_e.$$

The probability of the $1 \to 0$ transition can be written in its turn as follows:

$$P_{10} = A^{OT}_{10}\exp(-\Psi^{OT}_{10}). \tag{30}$$

Eqns. (29) and (30) make it possible to calculate the probabilities of transitions in the A + BC colinear collision. The task of the theory is now to employ the results obtained in order to calculate the rate constants for three-dimensional collisions and for the interpretation of the dynamics of these processes.

2. Model of a VR process

We shall now proceed to the consideration of a model for VR processes.

Recent studies on the mechanism of the vibrational relaxation on collision between an atom A and a highly asymmetric molecule BC (for example, a hydride molecule) made it possible to formulate a comparatively simple model[22] which is to some extent analogous to the Landau–Teller model. The probability of the loss of a vibrational quantum by the BC molecule not as a result of a single colinear collision with an atom A but during a single period of the rotation BC perturbed by the interaction with an atom A is calculated at the same modelling level. The probability of the transition found in this way is then used to calculate the rate constant for the three-dimensional collision in which the vibrational energy of the molecule BC is converted mainly into its rotational energy.

The semiclassical planar rotator model can be introduced as follows. Initially one considers the motion of the classical subsystem (the rotation of BC), which is described by the hamiltonian

$$H_{cl} = \frac{j^2}{2I} + A\cosh^{-2}\left(\frac{\delta\gamma}{2}\right), \tag{31}$$

where j is the angular momentum of the molecule (for a planar rotator, the variable j is coupled with the angle γ), $I = Mr_e^2$ the moment of inertia of the molecule BC (M is the reduced mass of the molecule BC and r_e its equilibrium internuclear distance). The transitions in the quantum subsystem (vibrations) are induced by a time-dependent perturbation of the type

$$V(x, t) = A\delta x A\cosh^{-2}\left[\frac{\delta\gamma(t)}{2}\right], \tag{32}$$

where the trajectory $\gamma(t)$ is found from the classical equations of motion with the hamiltonian (31).

In contrast to the hamiltonian (17), which describes a comparatively simple form of motion for any relation between the total energy E and the coefficient A (mutual approach of A and BC and their subsequent divergence—elastic one-dimensional scattering of the particle A by the rigid 'rod' BC), the hamiltonian (31) corresponds to a more complex type of motion. Namely, when $E > A$, the rotator BC executes hindered rotation and, when $E < A$, it librates. Accordingly, when $\gamma = 0$, the direction of motion of the rotator either does not change or it is reversed after the attainment of fairly small values of γ.

The semiclassical probability of the transition (again for simplicity one considers the transitions $n = 1 \to n = 0$) is described by the general formula (30), in which the exponent and the pre-exponential factor are expressed in terms of the parameters of the model and temperature. The principal corrections to the semiclassical probability of the transition are obtained by using the optimum trajectory method.

Somewhat more complex steps, but in principle analogous to those presented above, lead to the following expression for Ψ_{10}^{OT}:

$$\Psi_{10}^{OT} = \frac{2\pi r_e}{\hbar\delta}\left\{[2M(E_{r1}^* + \hbar\omega)]^{1/2} - [2ME_{r1}^*]^{1/2}\right\} + \beta E_{r1}^*, \tag{33}$$

where the optimum rotational energy E_{r1}^* is found from the equation

$$\frac{d\Psi_{10}^{OT}(E_{r1}^*)}{dE_{r1}^*} = 0. \tag{34}$$

In the case of VR processes, there exist, as in the case of VT processes, two simple limits in Eqn. (33)—at high and low temperatures. We shall not quote them, since they are fully analogous to Eqns. (26) and (27).

We may note two features of the model of VR processes under consideration.

One of them consists in the fact that Eqn. (33) retains the same form regardless of whether it describes the optimum libration trajectory or hindered rotation. This is extremely important because in the three-dimensional generalisation of the model the sharp difference between the two types of trajectory vanishes as a result of the influence of the centrifugal potential.

Another feature of the model of VR processes consists in the fact that the pre-exponential factor in the expression for the probability of the transition oscillates as a function of the rotational energy. This factor, which also exists for more complex models, hinders the averaging of the probability found in numerical calculations.[13] The oscillatory nature of the transition probability is related to the interference of two tunnel amplitudes: one associated with the initial branch of the optimum trajectory (from the turning point to the transition point) and the other associated with the final OT branch (from the transition point to the other turning point). Oscillations of this kind are absent from the Landau–Teller model, since the phase difference between the two transition amplitudes is extremely small in this model. The oscillations in the transition probability vanish after averaging with respect to energy. Such averaging can be achieved most simply within the famework of the OT method.

V. Energy exchange in three-dimensional collisions

Despite the wide-scale use of virtually exact computer calculations in the dynamics of molecular collisions, including the dynamics of the intermolecular energy exchange, the results obtained hitherto are of limited interest, since each refers to a definite potential energy surface selected on the basis of particular considerations. The use of approximate methods, which make it possible to follow comparatively simply the relation between the final result (the rate constant) and the initial parameters of the problem (the potential energy surface), is therefore of undoubted interest. In this section, we shall consider various approximate methods used in the vibrational relaxation and vibrational predissociation theory. The main task is to determine the relative contributions of the A–BC translational motion (taking into account the radial and relative rotational motions) and of the rotation of BC to the interaction inducing the vibrational transition. Significant progress in this respect has been achieved with the use of the OT method.

As mentioned above, the optimum trajectory is a multidimensional classical trajectory, which begins at the turning point of the relative motion in the initial vibrational state of the molecule and then extends over an imaginary time interval into the classically forbidden region of the potential, reaches the transition point, and, undergoing a discontinuity at this point, returns to the turning point in the final vibrational state of the molecule. The potential energy surface in the classically forbidden region is then constructed as an analytical prolongation of the surface from the classically allowed region. In the case considered this surface depends solely on two coordinates—the distance R between the atom A and the centre of gravity of BC and the angle γ between the axis of the molecule AC and the vector $\boldsymbol{R}$.

We shall consider initially VT processes. The main idea of the OT method in relation to VT energy transfer processes dates back to Takayanagy's 'modified quantum number method'[24] formulated for an isotropic potential. If the length $\mathscr{L}$ of the optimum trajectory (i.e. the distance between the turning points and the transition points) is small compared with the radius of curvature $\mathscr{R}$ of the equipotential line on the potential energy surface at the turning point, then one can carry out a local separation of the variables of motion in order to simplify the description of the collision dynamics. This approximation gives

rise to a one-dimensional 'reaction coordinate' directed at right angles to the constant energy surface; the remaining coordinates behave merely as 'observers'.

Thus the use of one-dimensional models for the description of the dynamics of three-dimensional collisions becomes possible. In particular, the Landau–Teller model is of this kind; its extension to three dimensions within the framework of the method indicated can be called the breathing shells model (the BSH model[15]). This model constitutes in its turn a generalisation of more approximate models: models based on the so called approximation of sudden perturbations relative to rotational transitions (the IOSA method[17]) and the breathing spheres model [the BSP model or the SSH model (after Schwartz, Slawski, and Herzfeld who first formulated it)]. In the last two models, the angle γ is assumed to be the 'observer' and the reaction coordinate is identified with the distance R. The BSH model identifies the reaction coordinate with a linear combination of R and γ. In order to apply the one-dimensional Landau–Teller model to the calculation of the rate constant for a three-dimensional collision, we specify a point with the coordinates R^* and γ^*, which is located on the potential energy surface:

$$U(R^*, \gamma^*) = E^*, \tag{35}$$

where E^* is the optimum energy. The probability of the Landau–Teller transition for the OT which begins at a turning point R^*, γ^*, assumes the form

$$\langle P^* \rangle = A(R^*, \gamma^*) \exp(-\Psi^*), \tag{36}$$

where the multiplier A and the exponent depend on R^* and γ^*. In particular

$$\Psi^* = 3\left(\frac{\theta^*}{T}\right)^{1/3}, \tag{37}$$

where $\theta^* = \omega^2\mu^*/2(\alpha^*)^2 k$ is the characteristic temperature of the model. In conformity with the BSH model,

$$\alpha^{\mathrm{BSH}} = \frac{|\mathrm{grad}\, U(R^*, \gamma^*)|}{U(R^*, \gamma^*)},$$

$$\mu^{\mathrm{BSH}} = \mu\left\{1 + \frac{(\mu/M)(R^*)^2(\mathrm{d}R^*/\mathrm{d}\gamma^*)^2}{[(R^*)^2 + (\mathrm{d}R^*/\mathrm{d}\gamma^*)^2] r_e^2}\right\}^{-1} \tag{38}$$

where r_e is the equilibrium internuclear distance in the diatomic molecule BC. The energy E^* is related to Ψ^* by the expression

$$E^* = \frac{\Psi^*}{3} kT, \tag{39}$$

whence follows the condition defining implicitly the optimum surface of the turning points $R^* = R^*(\gamma^*)$.

We now rewrite Eqn. (36) as follows:

$$P^{\mathrm{BSH}}(\gamma^*) = A^{\mathrm{BSH}}(\gamma^*) \exp[-\Psi^{\mathrm{BSH}}(\gamma^*)]. \tag{40}$$

The rate constant k^{BSH} is expressed in terms of $\langle P(\gamma^*) \rangle$ as the probability flux through the optimum surface of turning points:

$$k^{\mathrm{BSH}} = 2\pi \int_0^{\pi} \left(\frac{kT}{2\pi\mu^*}\right)^{1/2} (R^*)^2 A^{\mathrm{BSH}}(\gamma^*) \times \times \exp[-\Psi^{\mathrm{BSH}}(\gamma^*)] \sin\gamma^* \mathrm{d}\gamma^*. \tag{41}$$

It follows from the analysis[25] of the models mentioned above (BSH, IOSA, BSP) that only the first takes into account the dynamic contribution of the rotation of the BC model to the vibrational relaxation or predissociation process, because in terms of the IOSA and BSP approximations the angle γ is assumed to be constant throughout the period of the collision. The change in the angle γ during the motion of the system along the optimum trajectory does actually imply that the rotation participates dynamically in the energy exchange process between the vibrations and other degrees of freedom. It can be shown intuitively that for an interaction with a low anisotropy (for example, the collision of a homonuclear molecule with an atom), the dynamic contribution of the rotation is small. This is true in the sense that allowance for the rotation alters comparatively little (in relative terms) the exponent in Eqn. (16). However, even a small relative change in Ψ can alter appreciably the rate constant. In this sense, a small anisotropy can alter greatly the rate constant and the dependence of the latter on the principal parameters of the given problem is then the same as for the breathing spheres model or the collinear model. It is found that the contribution of the rotation is determined by the parameter Q, given by

$$Q = \frac{\mu(\Delta R)^2}{M r_e^2}, \tag{42}$$

where ΔR is the difference between the distances separating the turning points for the collinear and T-shaped configurations and M is the reduced mass of the molecule BC. This parameter enters into the exponent as a relative correction and hence the correction to the rate constant for rotation may be significant even when the parameter Q is very small. We may note that the parameter Q was introduced previously as a characteristic of the efficiency of the purely rotational excitation of molecules on collision with atoms.[26]

Thus the following type of temperature variation may be expected for the vibrational relaxation of homonuclear molecules at fairly high temperatures:

$$k_{10} = B \exp\left[-3\left(\frac{\theta^+}{T}\right)^{1/3}\right], \tag{43}$$

where θ^+ denotes the minimum of all the possible values of θ^* (the corresponding OT and its vicinity make the main contribution to k_{10}). The temperature variation of type (43) is known in the literature as the Landau–Teller law.

For further estimates, we resort to a simple formula for $(\theta^+/T)^{1/3}$:

$$\left(\frac{\theta^+}{T}\right)^{1/3} = 8.1\left[\frac{\omega/\mathrm{cm}^{-1}}{2000}\right]^{2/3}\left[\frac{\alpha/\text{Å}^{-1}}{4}\right]^{-2/3} \times \times \left[\frac{\mu/\mathrm{a.e.}}{10}\right]^{1/3}\left[\frac{T/\mathrm{K}}{1000}\right]^{-1/3}. \tag{44}$$

For typical values of ω, μ, and T ($\omega = 2000\ \mathrm{cm}^{-1}$, $\mu = 20$ a.u., and $T = 1000$ K) and the values of α in the expected range $3.5\ \text{Å}^{-1} < \alpha < 4.1\ \text{Å}^{-1}$, the parameter $(\theta^+/T)^{1/3}$ is of the order of 10. As a result, Ψ_{10}^{SC} is in the vicinity of 30, which explains the very low probability of vibrational relaxation in a single collision.

We shall now proceed to the consideration of VR processes. When the planar hindered rotator (HR) model is extended to the three-dimensional case, we shall assume that the angle γ is the reaction coordinate and R is the 'observer'. The parameters A and δ in the hamiltonian (31) are functions of R and the probability of the transition in the model case is averaged with respect to R. In such averaging, account must naturally be taken of the contribution of the isotropic interaction $U_0(R)$.

The general expression for the vibrational relaxation rate constant is

$$k_{10} = \left(\frac{8kT}{\pi I}\right)^{1/2} \pi s \int R^2\, \mathrm{d}R\, P_{01}^{\mathrm{HR}}(T, R) \exp[-\beta U_0(R)], \tag{45}$$

where s is the steric factor arising on passing from the planar rotation model to real three-dimensional rotation ($s < 1$).[27] The temperature variation of the rate constant defined by Eqn. (45) is described by Eqn. (43), in which θ^+ can be calculated by Eqn. (44), having replaced the reduced mass of the colliding pair by the reduced mass of the molecule and the radial potential gradient by the angular gradient:

$$\alpha \to \frac{\delta}{r_e}, \qquad \mu \to M. \tag{46}$$

The parameter δ, characterising the degree of anisotropy of the potential, varies in the range from 3 to 4 for hydrogen halide molecules.[6]

We may note in conclusion that the VT or VR type of any vibrational relaxation process is determined by the parameter Q: in the former case $Q \ll 1$ and in the latter $Q > 1$. In principle, there is a possibility of a situation where $Q \simeq 1$, i.e. when the relative A–BC motion and the rotation of BC are equally important in inducing the vibrational transition, but in systems of practical interest this is usually not encountered.

VI. Examples of vibrational relaxation and vibrational predissociation

Experimental study of vibrational relaxation under thermal conditions usually makes it possible to obtain information about the kinetics of the population of the lowest vibrational levels, from which it is comparatively difficult to extract the dependence of the relaxation rate constant on the number of the vibrational level. The corresponding data can therefore be used mainly for the elucidation of the dependence of the constants k_{10} on the dynamic and kinematic parameters of the partner species and also on temperature. We present below three examples illustrating the negligibly small, appreciable, and dominant contributions of the rotation of a diatomic molecule to the dynamics of vibrational relaxation.

1. Small contribution of rotation (VT process)

The breathing shells model and even its simplest limiting case—the breathing spheres model—describe comparatively well the experimental results of measurements of the rates of vibrational relaxation of homonuclear diatomic molecules in the heat reservoir of inert gas atoms (see, for example, a recent review[5]). As an example, we shall consider the vibrational relaxation of nitrogen in helium:

$$N_2(n=1, \text{thermal } j) + He \rightarrow N_2(n'=0, \text{all } j') + He. \quad (47)$$

In terms of the combination of masses, this system belongs to the light atom–heavy molecule type of system. For a system of this kind, the average collision time is short compared with the average period of the rotation of the molecule ($\mu/M \simeq 1/2$ and the parameter Q is very small). Fig. 2 illustrates the existing experimental data on the high-temperature and low-temperature vibrational relaxation of N_2 on He[28–30] and also the theoretical temperature dependence of the rate constant. The parameter α was chosen to be 3.8 $Å^{-1}$ in conformity with a non-empirical estimate.[31] The theoretical curve in Fig. 2 corresponds to the expression

$$k_{10}(T) = 1.6 \times 10^{-7}\left[\frac{T/K}{1000}\right]^{1/3} \times \times \exp\left\{-19.6\left[\frac{1000}{T/K}\right]^{1/3} + \frac{1680}{T/K}\right\} cm^3\,s^{-1}. \quad (48)$$

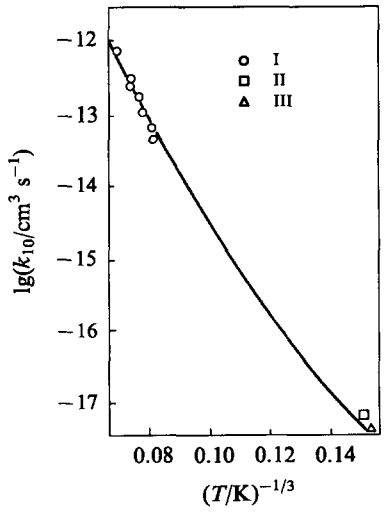


Figure 2. Temperature dependence of the rate constant for the vibrational deactivation of nitrogen by helium. Points I–III represent experimental data obtained in a number of studies.[28–30] Continuous line—results of calculation by Eqn. (48).

We may note the following interesting features of the temperature variation:

(a) The linear high-temperature part of the curve illustrates the Landau–Teller temperature variation [Eqn. (43)], which, as follows from the considerations presented above, permits a semiclassical interpretation.

(b) The low-temperature part of the curve resembles the Arrhenius plot for a chemical reaction rate constant which has been bent by tunnel effects. In this case the above analogy between the two processes is apt, since the curvature of the plot is due to quantum corrections to the semiclassical relation.

(c) The semiclassical approximation with the first quasi-classical correction can describe the variation of the relaxation rate constant over a range of more than six orders of magnitude, the lower limit of the range corresponding to temperatures which are much smaller than the characteristic vibrational temperature of N_2 ($\hbar\omega/k$ = 3360 K). The complete quantum description of the energy transfer process must be used below room temperature.

2. Appreciable contribution of rotation (VT process)

We shall now turn to another example—the vibrational deactivation of H_2 on collision with He. This system belongs to the class of light molecule–heavy atom systems and one may therefore expect an appreciable contribution of the rotation of the molecule to the rate of vibrational relaxation [we have the ratio $\mu/M \simeq 3$ and in this case the parameter Q is appreciably greater than for process (41) but is still less than unity]. However, experimental data for the vibrational relaxation of H_2 on He can be reasonably described within the framework of the IOSA model and even in terms of a rougher approximation—within the framework of the breathing spheres model.[5] The reason for this apparent contradiction is simple. For not unduly anisotropic potentials, a slight variation of the parameter α within the limits of its 'allowed' range of variation makes it possible to reconcile the simple model with experimental data without observing any defects of the model under these conditions. In order to observe the contribution of rotation, it is necessary to carry out a more detailed analysis of the dynamics. Such a problem has been solved and it has been shown[32–34] that an appreciable part of the energy evolved on vibrational deactivation is converted into the rotational energy of the hydrogen molecule. As an illustration of the importance of the rotational transitions accompanying the evolution of vibrational energy, we shall consider the deactivation process not under thermal conditions (equilibrium distribution with respect to translational and rotational energies) but under conditions where the initial energies of all the degrees of freedom are specified:

$$H_2(n = 1, j = 0) + He \rightarrow H_2(n' = 0, \text{all } j') + He. \quad (49)$$

The cross-section of this process is illustrated[35] in Fig. 3 as a function of the collision energy. It is seen from the figure that, when the dynamic contribution of rotation is ignored (the IOSA approximation or the breathing spheres model), then the cross-section is found to be smaller by an order of magnitude than the values obtained in the exact calculation. Analysis of the wave function for relative motion shows[29] that this difference between the cross-sections is induced by very small differences in the interaction potentials corresponding to different rotational states

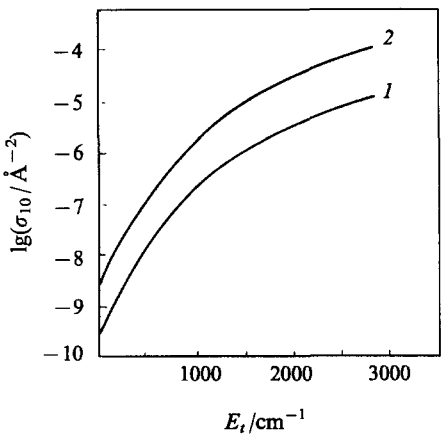


Figure 3. Dependence of the cross-section for the vibrational relaxation of hydrogen by helium on the collision energy:[35] (*1*) theoretical calculation without taking into account the dynamic contribution of the rotation of H_2 to the probability of the transition; (*2*) theoretical calculation taking into account the dynamic contribution of the rotation of H_2.

of H_2. Such a great sensitivity of the cross-section (or rate constant) to small variations in the potential is typical for tunnel processes in general and for dynamic modelling processes in particular.

3. A dominant contribution of rotation (VR process)

The process

$$\text{HF}(n = 1, \text{thermal } j) + \text{Ar} \rightarrow \text{HF}(n' = 0, \text{all } j') + \text{Ar} \tag{50}$$

may serve as an example of vibrational deactivation induced by the rotation of the relaxing molecule.

Experimental data[36–38] together with the theoretical relation,[6] obtained by fitting the hindered rotator model to various potential energy surfaces,[39,40] are presented in Fig. 4. In connection with this figure, we may note two factors. First, any attempt to interpret the experimental data within the framework of the BSP, IOSA, or BSH models would give rise to a discrepancy between the theory and experiment of several orders of magnitude. Second, the use for this system of various potential surfaces described hitherto in the literature leads to a greater scatter of the predicted rate constants compared with the error which is introduced when the planar rotator model potential is fitted to any surface. This illustrates yet again the fact that with the existing uncertainty in the calculations of intermolecular interactions accurate dynamic calculations provide comparatively little information.

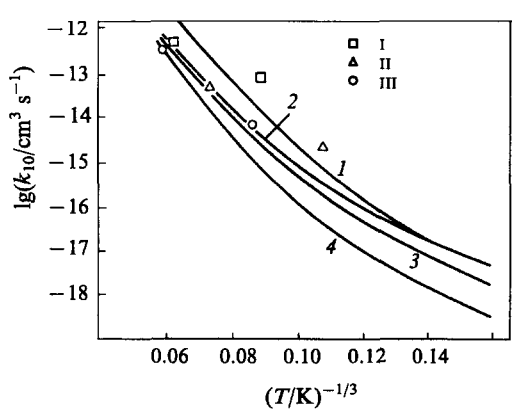


Figure 4. Temperature dependence of the rate constant for the vibrational relaxation of HF by collision with Ar: (I)–(III) experimental data obtained in Refs. 36–38 respectively; (*1*)–(*4*) theoretical calculations with the planar rotator model potential parameters determined for potential energy surfaces calculated in Refs. 39–41.

We shall now proceed to vibrational predissociation processes. In contrast to thermal vibrational relaxation, the study of vibrational predissociation makes it possible to test the dependence of the rate of predissociation on the number of the vibrational level n predicted by the theory, since laser excitation methods make it possible to synthesise the van der Waals complexes BC(n)...A with a wide range of values of n. In this respect, the predissociation of iodine–inert gas complexes, in particular the complex with neon, has been investigated in greatest detail:[42]

$$I_2^*(n)...\text{Ne} \rightarrow I_2^*(n-1) + \text{Ne}\,. \tag{51}$$

Fig. 5 presents the experimental results of the measurement of the rate of vibrational predissociation, which demonstrate a clearly non-linear dependence of the rate on n. This dependence can be fitted very satisfactorily by a function of type (29) and the gradient of the repulsive potentials $\alpha = 4.90\ \text{Å}^{-1}$ can be obtained from the parameters [we may note that this value is twice as high as the value of α quoted by Willberg et al.[42] because the repulsive branch of the Morse potential used in their study is described by the function $\exp(-2\alpha R)$]. The parameter α obtained in this way is only slightly outside the limits of the "expected" range (see above), which is associated simply with the errors of the model that uses a purely repulsive potential for the description of the transition from the bound to the dissociated state.

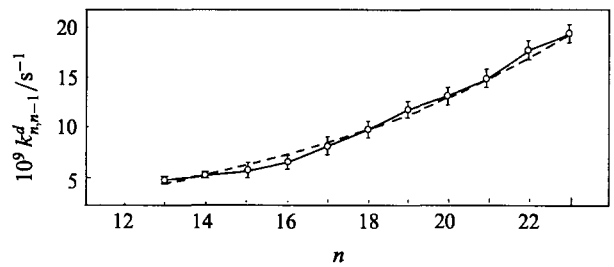


Figure 5. Dependence of the rate constant for the vibrational predissociation of the iodine–neon complex on the vibrational quantum number of the iodine molecule. The continuous curve connects the experimental points,[42] while the dashed curve represents the theoretical relation described by Eqn. (29).

VII. Conclusion

Dynamic tunnelling is a process which is forbidden in classical terms not because the initial and final states are separated by a high potential barrier but because the transition between these states is impossible by virtue of the adiabatic Ehrenfest principle. In the quantum formulation, this principle is expressed in the form of the claim that the probability of the transition betweeen the corresponding states is exponentially small. In many instances, and this applies particularly to vibrational relaxation and predissociation processes, this low probability can be associated with a non-adiabatic transition between two non-intersecting potential energy surfaces. Within the framework of the OT method, such a transition is described as the motion of the system along two trajectories and transition from one to the other takes place in the classically forbidden region of the potential. These trajectories are 'classical' in the sense that they are described by classical equations of motion; at the same time they are not classical in the literal sense because they characterise the motion of the system during an imaginary time. The latter is not a specific feature of dynamic tunnelling, since tunnelling

through a potential barrier can also be described as 'classical' motion in an imaginary time.

The method of optimum trajectories for the calculation of the vibrational relaxation rate constant examined above can be represented as an analogue of the transition state method in relation to the calculation of chemical reaction rate constants. Both methods are based on the same idea: instead of the traditional approach, based on the successive calculation of the probability of the process, its cross-section, and finally its rate constant, in this instance one calculates the average probability flux through the optimum critical surface. In this way, it is possible to avoid the search for the part of the information about the process dynamics which is always contained in the probability and the cross-section but which is lost on averaging with respect to the canonical ensemble in the stage involving the calculation of the rate constant. From this standpoint, the OT method can be regarded as a 'non-reaction' analogue of the so-called theory of reduced dimensionality for the calculation of the rates of 'reaction' events. The latter approach proved extremely fruitful in the theory of chemical reactions.[43-45]

Just as the transition state method makes it possible to calculate the pre-exponential factor for the reaction rate constant in the form proposed by Arrhenius, the optimum trajectories method permits the calculation of pre-exponential factor for the relaxation rate constant in the form proposed by Landau and Teller. At the same time, it is clear that the method of optimum trajectories can be criticised to the same extent as the transition state method: the fundamental question under what conditions the canonical distribution with respect to the degrees of freedom of species before collision can be 'transferred' to the critical surface, which is in the region of their interaction, cannot be regarded as fully solved at the present time.

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