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Energy exchange and reactions of highly excited polyatomic molecules

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Abstract. The advances in the study of energy exchange in the reactions of highly excited polyatomic molecules are analysed. The possibilities of spectroscopic methods for the observation of nonequilibrium energy distributions are demonstrated. Various models of intramolecular and intermolecular energy exchange as well as the reactions of highly excited states of polyatomic molecules are considered: spontaneous unimolecular decomposition and bimolecular reactions. Application of emission techniques in the visible, UV and IR spectral regions, both in the traditional version and especially with Fourier transformation, is very effective for detection of distributions of highly excited states in reacting systems with thermal and laser pumping. Several predictive comments are made in conclusion. The bibliography includes 130 references.

I. Introduction

The history of chemical kinetics is indissolubly linked with the reactivity of highly excited molecules.[1–3] The rates of the vast majority of reactions depend significantly on the fraction of species where the internal degrees of freedom contain an amount of energy comparable to the reaction threshold E_0 or the barrier E_d separating the electronic configuration of the products from that of the reactants.

In the case of highly excited molecules, the number of species capable of reacting is determined by the simultaneous influence of many elementary processes — nonelastic scattering (energy exchange), collisions with rearrangement (chemical reactions), and interactions with external fields.

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The macroscopic experimentally measured rate constant has an internal structure reflecting the relationship (frequently sophisticated) between the energy exchange processes and chemical reactions. The first and hitherto unsurpassed advance in the elucidation of this internal structure is the statistical theory of unimolecular reactions.[4–8] By virtue of the distinct physical basis and the high degree of development of the computational methods, this theory has found so many applications that it has stimulated the extension of the 'unimolecular ideology' to the entire wide variety of bimolecular reactions. The achievements in this field are illustrated in the present review.

In the case of rapid energy exchange, the distribution of the reactants with respect to rates and energy levels corresponds to equilibrium. Under these conditions, the kinetics of chemical reactions are described by equations for concentrations which include the rate constants averaged thermally and the reaction rates are determined solely by the pressure, temperature, and mixture composition.

The development of experimental techniques and the requirements of modern technology have favoured a shift of the interest of investigators into the field of study of rapid reactions, which not only compete with energy exchange processes and processes involving the establishment of distributions but under certain specific conditions fully determine the form of these distributions.

For molecules with a small number of atoms and low excitation energies, the necessary information about the elementary processes is usually obtained in beam experiments, with laser methods for the generation of beam species in well defined quantum states and laser methods for the observation of the states of the product species.

By virtue of the progress in the development of computational techniques in quantum chemistry and in atomic collision theory, it has become possible to obtain reliable information about the elementary processes also by purely computational methods.[5,6] For polyatomic and highly excited molecules, these methods are being used with increasing frequency and the reviews in this field therefore rapidly become obsolete.

Molecular spectroscopy has exerted a definite influence on the establishment of the fundamental concept associated with molecular structure. The 'kinetic' aspect appeared in this field in

connection with the study of the absorption spectra of unstable species. The direct kinetic application of spectroscopy involves the analysis of the width of spectral lines. The CH_3 radical may serve as a characteristic example. Its predissociative line width of 60 cm^{-1} in the 216 nm absorption band [9,10] may be assigned to a predissociative lifetime of $\sim$ 88 fs (for CD_3, the corresponding values are 8 cm^{-1} and 663 fs, which can be accounted for by the considerable isotope effect). After four decades of experimental studies in this field, the number of examples of this kind has increased greatly and the range of lifetimes extends from femtoseconds to microseconds.

Later examples, associated with molecular dynamics, include nonradiative transitions in polyatomic molecules (see, for example, Jortner and Bixon [11]) and also the interaction of coherent laser radiation with molecular systems.[7,12,13]

Analysis of the possibilities of spectroscopic methods together with the description of their applications to specific systems represents the main content of the present review.

II. Molecular kinetics and molecular spectroscopy

The extensive introduction of spectroscopic methods into chemical kinetics during the last 30 years has completely altered its features and has caused a shift in priorities. The subdivision of the methods of study employed into 'direct' and 'indirect' has little justification. Firstly, there are no methods which would yield kinetic information without interpretation within the framework of some kind of model. Secondly, the systemic approach with analysis of the entire available information is the most productive.

The true history of any science is the history of concepts. In this respect too, the kinetics of unimolecular reactions yield a striking example of the way that the use of indirect methods has created a firm basis, which was merely strengthened on subsequent application of the entire available range of modern optical spectroscopic techniques.

In fact, all the principal concepts constituting the foundation of the modern theory of unimolecular reactions have been formulated on the basis of experiments carried out by traditional methods of chemical kinetics:[4] the identification of the stages involving activation and spontaneous decomposition of the active molecules; the concept of a quasi-continuum of vibrational-rotational states: the correct estimation of the intramolecular relaxation time of the vibrational energy of active molecules.

Paradoxically, after the discovery of the IR laser-induced dissociation of polyatomic molecules, many efforts were wasted on attempts to interpret the results within the framework of modified one-oscillator models before it was recognised that the principal results fit within the framework of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory, which had already been used by kineticists for many years.

1. Models of polyatomic molecules for kinetic applications

Qualitatively new features, consisting of an increase in the density of states and a considerable acceleration of the energy exchange between them, arise in polyatomic and highly excited molecules. As a consequence of the rapid intramolecular energy exchange (electronic-vibrational conversion, intermode transitions, or rotational-vibrational exchange), with increase in the excitation energy the simple picture of motion, characteristic of molecules with a small number of atoms or weakly excited molecules, disintegrates. The energy spectrum becomes much more complex because vibrational motion becomes stochastic.[7]

A high degree of specification of details in the description of the structure of a polyatomic molecule is not required for kinetic applications or for the interpretation of the results of measurements with a moderate spectroscopic resolution. Fig. 1 presents the simplest scheme, which clearly illustrates the majority of the phenomena discussed in the present review. A 'spaced out' vibrational spectrum in the lower parts of the ground and electronically excited terms, transforms into a quasi-continuum with rapid

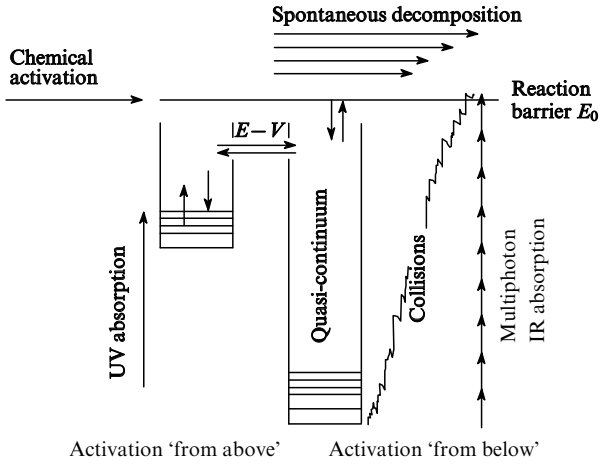


Figure 1. Principal kinetic processes in the activation of a polyatomic molecule.

mixing of the vibrational modes. The types of activation ('from below' and 'from above') are indicated. The vertical arrows designate the collision and vibrational-translational ($V-T$) transitions, whilst the horizontal arrows designate chemical reactions: on the left — activation as a result of exothermic chemical reactions, on the right — spontaneous decomposition, which intensifies with increase in the vibrational energy; $E-V$ represents the electronic-vibrational exchange between the terms.

Any external influence on the molecular system leads rise to a nonequilibrium distribution with respect to energy levels, the form of which is determined by the competition between the pumping and relaxation processes and chemical reactions.

The methods for the interpretation of non equilibrium energy distributions have also developed in parallel with the development of diagnostic methods in relation to highly excited states (HES). In this connection, it is instructive to turn to the hierarchical picture of the models of nonequilibrium processes (specifically, we have in mind the unimolecular decomposition reactions):

the two-level Lindemann scheme for unimolecular decomposition deals with the ground state of a polyatomic molecule and its excited (active) state in the region of the barrier to chemical reactions; this model operates with the corresponding kinetic equations for the concentrations of above states and yields a level of description necessary for the interpretation of macroscopic rate constants;

the model based on the use of the concept of the vibrational temperature T_v for a separate ensemble of vibrational degrees of freedom, which, generally speaking, is not in equilibrium with the surrounding gas at a temperature T_g; in fact, in this description the form of the nonequilibrium distribution function is assumed to be identical with the Boltzmann distribution; in order to find T_v, the system of chemical kinetic equations is supplemented by the balance equation for the vibrational energy and then the rate constant for unimolecular decomposition is a function of two temperatures — T_v and T_g;[10–17]

intepretation of kinetics 'in the language' of the distribution function with respect to the internal energy of molecules; the experimental data are analysed using the solution of the fundamental microkinetic equation [(FME) — master equation].

With the aid of Fig. 1, it is convenient to elucidate the sense of the term 'highly excited states' of polyatomic molecules. In the context of the current review, these are states for which there is no possibility of subdividing vibrations into modes and the energy of which is consequently higher than the threshold of the transition of vibrational motion to the stochastic regime.

2. Spectroscopic methods for the study of highly excited molecules

Highly excited states of molecules with average energies $\langle E \rangle \simeq E_0$ may be obtained as a result of the thermal heating by a shock wave, single photon optical excitation with subsequent intramolecular $E-V$ conversion, or multiphoton excitation in the field of intense IR radiation, electron impact, *etc.*[14–16]

Mainly optical methods are used for the recording of HES and for the observation of energy distributions, although others, for example corpuscular or field methods, may also be useful. There are many versions of optical methods, for example the absorption and emission methods, in which the radiation in various wavelength ranges (IR, visible, UV) is used. The optical methods are characterised by a high time resolution and yield the most complete information about the evolution of intramolecular and intermolecular energy distributions.

The methods for the study of the collision deactivation of the HES of polyatomic molecules may be divided into two groups. The methods of the first group are used to record processes associated with the highly excited molecules themselves, whilst those of the second group record the responses of the surrounding system to the HES relaxation process. The thermal lens[17] and optoacoustic methods have been used to find the energy flux from the HES to the translational degrees of freedom in the course of relaxation.[9,18] The methods involving the recording of the HES themselves belong to the group of methods with the highest information content.

3. Characteristic features of the principal methods for the generation of HES

The advantages and disadvantages of various methods for the generation of HES are determined by the degree of their universality, the range of available energies, and the possibility of the establishment of HES distributions of a specified type. The types of activation considered below are illustrated in Fig. 1.

The thermal heating method, which can be readily applied in experiments with shock waves, is one of the most universal. It makes it possible to achieve a virtually instantaneous heating of molecules to temperatures of several thousands of degrees.

The method involving the resonance multiphoton IR excitation of polyatomic molecules has come to be widely employed immediately after the appearance of CO_2 pulse lasers.[7,9,12,13] At the present time, the physics of the interaction of the intense IR radiation with polyatomic molecules has been examined in numerous publications in which all the principal features of this method for the study of the spectra and reactions of HES are dealt with. The resonance pumping of molecules by an IR laser in the pulse regime makes it possible to obtain HES over a period $t \simeq 10^{-8}$ s, whereupon the molecules form two ensembles — 'cold' and 'hot'. (The temperature of the latter may reach thousands of degrees.)

The single-photon UV excitation method (with subsequent intramolecular $E-V$ conversion) is used to generate the HES of molecules having an electronically excited state in the range of energies investigated. This state is mixed by a nonadiabatic interaction with the high vibrational levels of the ground state. Typical examples of such molecules are SO_2 and NO_2. The energies of the initial excitation, accessible to the resonance single-proton UV excitation method, are of the order of several electron-volts. The initial energy distributions of the HES are close to the δ-distributions and may be regarded as microcanonical.

4. Molecular spectroscopy and the development of methods for the study of highly excited states

Molecular spectroscopy is one of the principal methods yielding information about the dynamics of processes involving the HES of polyatomic molecules. Bearing in mind the special interest in the purely chemical aspects of such processes, we have given preference to the absorption-emission diagnostics based on moderate spectral resolution with a characteristic time range of $0.1-1000$ μs.

If an external perturbation induces a jump in one or several parameters (temperature, pressure, electric field strength, or another macroscopic parameter), then the subsequent evolution of the system towards an equilibrium state (or most often a quasi-stationary state) can be monitored by classical kinetic spectroscopic methods.[2,7,9]

The time resolution of flash photolysis has increased during the last 30 years from microseconds to femtoseconds and, when combined with coherent spectroscopic methods in the femtosecond range, this makes it possible to follow the real dynamics of the formation and dissociation of chemical bonds.

In contrast to the classical kinetic spectroscopic technique, which is designed primarily for the investigation of the so called global reaction mechanism and the corresponding rate constants, the modern technique employing laser methods in molecular beams with coherent nanosecond and femtosecond pulses, leads to the possibility of the observation of the detailed features of molecular dynamics.[19,20] Several scientific centres, particularly those with the necessary financial resources, are leaders in research of this kind.†

5. The method of competing channels with application of fluorescence spectroscopy

The initial concepts of the method of competing channels using fluorescence spectroscopy arose in relation to proton and electron transfer processes in solutions.[20] Later this method came to be widely employed for the study of intramolecular kinetics and of the redistribution of vibrational energy in electronically-excited states of polyatomic molecules.[21,22] An essentially analogous approach has been applied in experiments with chemical activation and intramolecular relaxation[23] under the conditions of stationary photolysis at high pressures,[24] where collisions in a gas are used as a time reference standard ('clock'). However, it is not always easy to answer the question which particular competing channels have to be considered in interpreting the results.

6. The line form in optical spectra

The Lorentzian optical line width Γ in optical spectra may be related to the rate constant k for a quasi-unimolecular process by the simple equation

$$k = \frac{2\pi\Gamma}{\hbar},$$

where $\hbar$ is the Planck constant.

Predissocation and similar processes are suitable examples of the applicability of this approach. The same method has been used to record high overtones for polyatomic molecules under beam conditions in order to obtain information about the rates of relaxation processes,[25,26] but it is then necessary to take into account very thoroughly the contributions of the uniform and nonuniform line broadening.[27,28]

Detailed analysis of the experimental methods used to investigate the dynamics of the HES of polyatomic molecules is an object of separate detailed consideration. In this communication, these methods will not be dealt with. In order to obtain an idea about the modern diagnostic possibilities, one may refer to monographs and reviews.[9,12,13,29]

Amongst spectroscopic methods, the laser methods involving molecular beams with application of the Fourier transformation

† The experimental technique has become so complex in this case too that the maintenance of a prestige level of research has become more of a contest between capacities for investment rather than between concepts. Furthermore, one should note also a degree of uncertainty in the interpretation of the results of measurements with ultrashort pulses — the rate of some kind of fast process is measured but it is sometimes not understood which particular process this is.[9]

of the spectra are correctly regarded as the most fruitful for the study of processes with participation of HES.

The possibilities of various optical methods for the probing of molecules and radicals using laser radiation sources have been described in fair detail in reviews.[9,29] The high spectroscopic resolution of these methods makes it possible to employ them for the detection of species in fixed quantum states, but in the study of the kinetics of energy exchange, unimolecular decomposition, and bimolecular reactions the simpler and at the same time fairly informative absorption methods with a moderate spectral resolution are preferable. These methods have in fact proved to be the most convenient to obtain the isoenergetic distributions $f(\langle E \rangle)$ which enter into the fundamental microkinetic equation (FME).

III. Molecular 'hot' band absorption spectroscopy

1. Fundamental relations

It is known that the UV absorption spectra of many polyatomic molecules have the characteristic form of bell-shaped curves with temperature-dependent moments.[10,30] With increase in temperature, the spectra shift towards the long-wavelength region and are broadened; a molecular 'hot' band is then said to be produced. It is related to the increase in the population of the excited molecules (Fig. 2).

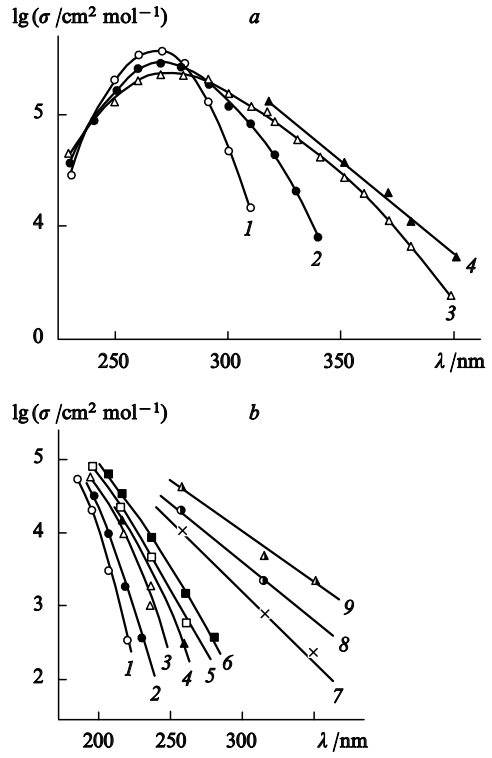


Figure 2. Dependence of the absorption cross-section for the 'hot' bands of the CF_3I (*a*) and N_2O (*b*) molecules on the wavelength.
T(K): *a*: (*1*) 300; (*2*) 625; (*3*) 1050; (*4*) 1250; *b*: (*1*) 300; (*2*) 470; (*3*) 670; (*4*) 770; (*5*) 870; (*6*) 950; (*7*) 1430; (*8*) 1620; (*9*) 2070.

The 'quasi-diatomic' molecule model, with the linear-oscillator fitting of the terms between which a vertical transition takes place following the absorption of a photon, is used for the simplest interpretation of these spectra. Subject to additional hypotheses concerning the nature of the fitting [31] of the wave functions for the dissociated states of the electronically excited molecule and the independence of the transition point of the vibrational energy of the initial state, the linear-oscillator model of the vertical transitions leads to the well known Wieland – Sulzer formula [32]

$$\sigma(v,\ T) = \sigma_0 \mathrm{th}\left(\frac{\theta}{2T}\right)^{1/2} \exp\left[\mathrm{th}\left(\frac{\theta}{2T}\right)\left(\frac{v - v_0}{\Delta v}\right)^2\right]. \qquad (1)$$

Here σ $(v,\ T)$ is the experimentally measured absorption cross-section, σ_0 a phenomenological parameter, θ the vibrational quantum of the oscillator, v the optical transition frequency, v_0 the frequency of the vertical transition from the equilibrium position, $\Delta v = F^2/\mu\theta$, F the strength of the interatomic interaction in the dissociated state, and μ the reduced mass.

Formula (1) describes fairly well the form of the main part of the absorption spectrum, but it does not take into account the weak but experimentally clearly observed shift of the maximum of the absorption curve.[32,33] The temperature dependence of the absorption cross-section can be obtained if account is taken in the calculation of $\sigma(v,\ T)$ of the anharmonicity of the vibrations, the curvature of the form of the electronically excited state, or the dependence of the electronic matrix element on the interatomic coordinate.[34,35] Here it is also possible to eliminate the systematically observed discrepancy between theory and the measured quantities in the long-wavelength region.

For the Morse exponential model, the parameters of the interaction potential are expressed by the relations

$$U_i(R) = D[1 - \exp(-\alpha R)]^2,$$

$$U_f(R) = A\exp(-\beta R) + \Delta,$$

$$M_{if}(R) = M_{if}(0)\exp(\alpha R).$$

where D, α, A, β, and Δ are the parameters of the potential in the initial (i) and final (f) states as a function of the interatomic distance R (the numerical values for the CF_3I molecule have been published [34]), U_i and U_f are the electronic terms of the molecule before and after the absorption of a photon, and M_{if} is the electronic matrix element.

The Gaussian fit to the central part of the absorption spectrum (*i.e.* the generalised Wieland – Sulzer formula) was first obtained by Dalidchik *et al.*[34] It was established that the first moments of the absorption spectrum are a little 'sensitive' to the form of the distribution of the molecules with respect to vibrational levels, but do depend on the dynamic parameters of the model and on the average energy of the initial excitation $\langle E \rangle$. Optical measurements in the central part of the absorption spectrum may be used either for the determination of the parameters of the potential curves or for the measurement of the first moment of the vibrational energy distribution function.

Numerous examples of the measurements of $\langle E \rangle$ based on the UV absorption spectra have been published by Troe and coworkers,[14,36–39] Letokhov and coworkers,[12,40–42] and other investigators.[43,44] However, the possibilities of UV absorption spectroscopy are not restricted solely to the measurement of the average excitation energy. It has been shown [45] that the long-wavelength edges of the absorption spectra of CF_3I and N_2O exhibit a distinct Arrhenius relation:

$$\sigma(v,T) \simeq \exp\left(-\frac{E_a(v)}{T}\right),$$

where $E_a(v)$ is the activation energy, which decreases monotonically with increase in the photon frequency v.

Within the framework of the one-dimensional model, *i.e.* in terms of the 'quasi-diatomic molecule' approximation, such relations can be understood if use is made of the concept of vertical transitions between classical turning points.

The classical approximation may be used if the contributions of the ground and weakly excited vibrational states are negligible at the given absorption frequency. The corresponding criteria, quoted by Dalidchik *et al.*,[34] usually hold in the long-wavelength region.

In the classical approximation for the one-dimensional model, the average photoabsorption cross-section assumes the form [34,35,46]

$$\sigma(v) = \frac{4}{3}\pi v \mathrm{f}\{U_i[R_0(v)]\}\,|\{M_{ij}[R_0(v)]|^2[U_i'(R_0) - U_f'(R_0)]. \quad (2)$$

Here $\mathrm{f}(U_i)$ is the normalised distribution of molecules with respect to vibrational energy and $R_0(v)$ is the root of the equation

$$U_i(R) + v = U_f(R), \quad (3)$$

where U_f is the potential energy surface for the electronically excited state of the molecule.

The results of absorption measurements in the long-wavelength region are related directly to the vibrational energy distribution of molecules [see Eqn (2)].

Eqns (2) and (3), which demonstrate the possibilities of the UV absorption technique, can be applied directly only in the case of diatomic molecules. On the other hand, experiment has shown that, for a reasonable parametrisation Eqns (2) and (3) can be used successfully also for the interpretation of the UV absorption spectra of more complex molecules such as those of CS_2,[36] N_2O,[45] SO_2,[47] *etc*.

When the spectra of complex molecules are described in terms of the formulae of the one-dimensional model, the theory of the UV absorption method is faced by the fundamental question of the physical significance of the concept of the 'optically active' oscillator in the most general form.[46]

The multidimensional generalisation of formula (2) assumes the form

$$\sigma(v) = \sigma^0 \mathrm{f}\{U_i[R_0(v)]\}\,, \quad (4)$$

where σ^0 is a known multiplier which varies little, quoted by Dalidchik *et al.*,[46] U_i the potential energy surface of the molecule in the initial electronic state, and $R_0(v)$ the trajectory of the coordinate of the absolute minimum of the function $U_i(R)$ on the hypersurface $\sum(v)$, satisfying the condition for the classical vertical transition (3) (R is the set of all vibrational coordinates).

For equilibrium conditions,

$$\mathrm{f}(U_i) = N\exp\left(-\frac{U_i}{T}\right),$$

i.e. the role of the 'activation energy' for the absorption spectrum is assumed by the function $U_i\,[R_0(v)]$.

Having compared Eqn (4) with the corresponding classical expression for the one-dimensional model, it is possible to elucidate the significance of the concept of the 'optically active' oscillator. In the vicinity of the extremum, $v = v_0$, where v_0 is the root of the equation

$$\frac{\mathrm{d}}{\mathrm{d}v}U_i[R_0(v)] = 0\,,$$

the function $\mathrm{f}\{U_i[R(v)]\}$ may be fitted by a Gaussian function. For agreement with the results based on the one-dimensional model, it is then sufficient that the following simple condition should hold:

$$\frac{\mathrm{d}^2}{\mathrm{d}v^2}U_i[R_0(v)] = 0\,.$$

The 'optically active' oscillator is identical with the nth normal oscillator if the trajectory of the point $R_0(v)$ lies in a plane which is sufficiently close to the oscillations plane of the nth normal oscillator.[34, 35]

Experimental data (Fig. 2) as well as the results of the numerical solution of Eqn (4) for the two-dimensional model of the photodissociation of the CF_3I molecule [46, 48] have shown that, in the photodissociation of this molecule, the conditions for which the quasi-diatomic approximation may be applied holds satisfactorily (at any rate for $\lambda > 300$ nm), so that the 'optically active' oscillator may be identified with the stretching vibration of the C–I bond.

The formalism developed for the description of 'hot absorption bands' has in the main proved suitable also for the description of the characteristics of heated molecular gases. The possibilities of the emission diagnostics for HES have been clearly demonstrated [45] and are also briefly considered below in connection with the survey of the results of the study of the wave characteristics of the relaxation of the HES.

2. 'Calibration' of absorption and emission spectra

The main result of the above analysis of 'hot' absorption bands is that the absorption cross-section for the far wing is proportional to the HES population [Eqns (2) and (4)]. However, the effectiveness of a specific application of the relations obtained depends in many respects on how well the disposition of the terms is known. The exact knowledge of these parameters is an exception rather than the rule. The role of the empirical information about the temperature and frequency dependences of the absorption cross-section for the test molecules therefore increases.

A sufficiently complete amount of information of this kind is obtained when shock-wave heating is employed. The essential feature of the approach, developed by Zaslonko and coworkers,[45, 46] reduces to the following. It is necessary to measure the relation $\sigma(v, T)$ at temperatures and pressures which guarantee the equilibrium distribution with respect to energy. The principal factor which prevents the maintenance of equilibrium is the reaction of the HES in the region of chemical reaction barriers. For unimolecular decomposition, equilibration implies that the reaction occurs at the high pressure limit, whilst for bimolecular processes this entails the occurrence of the reaction at low concentrations of the reactants whereupon the distorting influence of the reaction is minimal.

Thus when equilibrium has been attained, the equation for the absorption cross-section 'activation energy' can be represented in the following form:

$$E_i = E_\upsilon + \overline{E}_\mathrm{v} + \overline{E}_\mathrm{r}\,,$$

where E_i is the energy of the vibrational state, E_υ the absorption cross-section activation energy, and $\overline{E}_\mathrm{v}$ and $\overline{E}_\mathrm{r}$ are the average vibrational and rotational energies of the excited molecule.

The dependences of the energy levels of the excited states, obtained in the calibration of the 'hot' absorption bands and on the basis of the thermal emission of SO_2 and NO_2, on the transition wavelength are presented in Fig. 3. Evidently the combination of the absorption and emission methods is applicable to a wide range of energies of the excited states. Here we are dealing with differentiated optically active states. In order to apply these methods in the kinetics of nonequilibrium processes, it is necessary to find the relation between the population of optically active molecular states and total vibrational energy of the molecules.

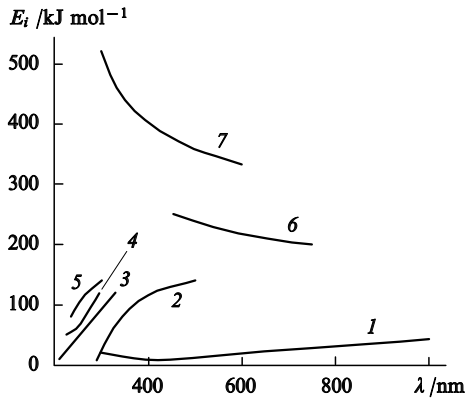


Figure 3. Dependence of the recorded excitation energy of the optically differentiated states of some molecules on the transition wavelength. Absorption: (*1*) NO_2; (*2*) SO_2; (*3*) N_2O; (*4*) CS_2; (*5*) CO_2; emission: (*6*) NO_2; (*7*) SO_2.

IV. Relation between the partial and total distribution functions with respect to the vibrational energy of polyatomic molecules

It is necessary to emphasise the differences in the description of processes involving HES in spectroscopy and kinetics. In kinetics, the principal parameter is the total HES energy, whilst in spectroscopy it is the population of an optically active oscillator or group of oscillators.

The vibrational energy distributions obtained on the basis of the analysis of the 'hot' bands in the absorption-emission spectra, refer to an optically active vibration of the molecule. In contrast to the distribution function (DF) with respect to the total energy, such distributions will be referred to as partial (PDF). The total number of independent partial distributions is equal to the number of normal vibration modes in the molecule.

In the solution of problems in chemical and molecular kinetics, we are as a rule interested in the distribution with respect to the total energy. In this connection the problem of finding the DF with respect to the total energy from spectroscopic PDF measurements arises.

The method for the finding of a relation between the PDF and the DF [49] is based on the hypothesis that, during the period of the observation of the PDF, there is sufficient time for the total energy of the molecule to be randomly redistributed between all the types of vibrations of the polyatomic molecule.‡ The probability of observing a molecule with an energy E_i of a differentiated type of vibration for the total energy E is specified by the conventional distribution $\varphi(E_i|E)$, which is proportional to the number of states accessible for the specified E and E_i:

$$\varphi(E_i|E) = \frac{\rho_i(E_i)\rho_{s-i}(E-E_i)}{\rho_s(E)}\,.$$

Here $\rho_i(E)$ and $\rho_{s-i}(E-E_i)$ are respectively the densities of states of the differentiated (i) and remaining ($s-i$) oscillators of a polyatomic molecule in which the number of modes is s and $\rho_s(E)$ is the total density of states of a molecule with a total energy E.

In order to obtain the partial distribution function $f_i(E_i)$, it is necessary to average $\varphi(E_i|E)$ with respect to the total energy distribution $f(E)$:

$$f_i(E_i) = \int_{E_i}^{\infty} \varphi(E_i|E) f(E)\,dE\,. \qquad (5)$$

Eqn (5) serves as a basis for the reconstruction of the DF from the experimentally measured PDF, since it establishes a mutually unambiguous relation between them.

It is convenient to express Eqn (5) in terms of the dimensionless Boltzmann distributions $f_{i0}(E_i)$ and $f_0(E)$ and the functions $h_i(E_i) = f_i(E_i)/f_{i0}(E_i)$ and $h(E) = f(E)/f_0(E)$. The Boltzmann distribution is specified in the form

$$f_0(E) = \frac{\rho(E)}{Q}\exp\left(-\frac{E}{RT}\right),$$

where $\rho(E)$ is the density of the spectrum and Q the vibrational partition function.

Taking into account this relation, we express Eqn (5) in the form

$$h_i(E_i) = \frac{Q_i(T)}{Q_S(T)}\int_{E_i}^{\infty} h(E)\rho_{s-1}(E-E_i)\exp\left(-\frac{E-E_i}{RT}\right)dE\,, \qquad (6)$$

where Q_i and Q_s are respectively the partial and total vibrational partition functions.

‡ This hypothesis is valid for energy levels higher than the barrier to the state where the vibrational energy becomes stochastic.

It is useful to examine certain limiting cases. In particular, it follows from Eqn (6) that, if the distribution with respect to total energy corresponds to equilibrium [$h(E) = 1$], then the PDF also corresponds to equilibrium [$h_i(E_i) = 1$]. In the other limiting case for the δ-distribution, $f(E) = \delta(E-E^*)$, where E^* is the total excitation energy, the PDF is defined by the microcanonical distribution

$$f_i(E_i) = \varphi(E_i|E^*)\,.$$

The relation between $f(E)$ and $f_i(E_i)$ is found from the integral transformation of Eqn (5). In the general case, this cannot be done analytically. If the Whitten – Rabinovitch approximation [4] is used for the density of states, *i.e.*

$$\rho_n(E) = \frac{[E + a_n(E)E_{z_n}]^{n-1}}{(n-1)!\prod\limits_n \hbar\nu_n}\,, \qquad (7)$$

where $a_n(E)$ is a parameter close to unity and is weakly dependent on E [4, 8, 50] and

$$E_{z_n} = \frac{1}{2}\sum_{k=1}^{n}\hbar\nu_k,$$

is the energy of the zero-point vibrations of n vibrational modes of the molecule, then the problem may be solved.

For sufficiently high values of the total energy, it is possible to neglect the energy of the zero-point vibrations in Eqn (7). The integral Eqn (6) may be solved with the aid of the Laplace transformation.[4] Direct substitution of the equation

$$h(E) = \frac{(s-i)\prod\limits_k \hbar\nu_k Q_{s-i}}{Q_i}\left(\exp\frac{E}{RT}\right)(-1)^{s-i}\times$$

$$\times\,\frac{d^{s-i}}{dE^{s-i}}\left[h_i(E)\left(\exp\frac{-E}{RT}\right)\right],$$

in Eqn (6) makes it possible to make sure that the former is a solution of the integral Eqn (6).

For example, for a molecule in which the number of oscillators is $s = 3$, we have

$$h(E) = h_i(E) - 2RTh_i'(E) + (RT)^2 h_i''(E)\,.$$

Evidently the total DF is defined not only by the absolute value of the PDF but also by the $s-i$ derivatives of the functions $h_i(E)$, *i.e.* it depends on the number of oscillators in the polyatomic molecule. The reconstruction of the DF on the basis of the PDF therefore requires definite types of fitting of the experimentally measured PDF.

We shall examine specific distributions obtained on thermal heating of polyatomic molecules in shock waves. Fig. 4 presents the results of the measurements of the PDF for the CF_3I, N_2O, and CO_2 molecules obtained by absorption methods and the reconstruction of the DF on the basis of the total energy is illustrated in Fig. 5. In particular, for the CF_3I, N_2O, and CO_2 molecules, a satisfactory fit to the measured PDF is provided by the function

$$h_i = 1 - C\exp\frac{E_i}{\gamma}\,,$$

where C and γ are the constants determined in the fitting process.

The examples presented indicate the scale of the 'depletion' of the DF in the vicinity of the chemical reaction barriers. Further analysis of the DF within the framework of the solution of the fundamental microkinetic equation (FME) makes it possible to obtain quantitative information about the mechanism of the activation of a highly excited polyatomic molecule and about its reactivity.

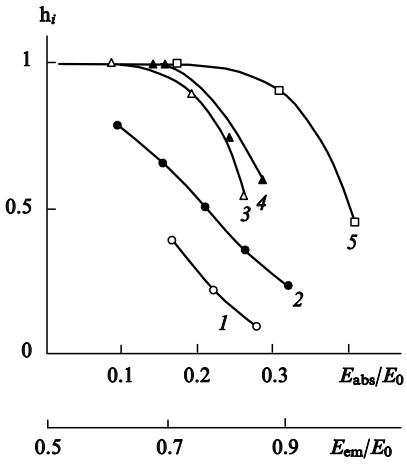


Figure 4. Dimensionless PDF with respect to the vibrational excitation energy of molecular states in reactions behind shock waves: (*1*) SO_2; (*2*) NO_2; (*3*) CF_3I; (*4*) CO_2; (*5*) N_2O; E_0 — reaction barrier: E_{abs} and E_{em} — excitation energies of the optically differentiated degrees of freedom measured by absorption and emission methods respectively.

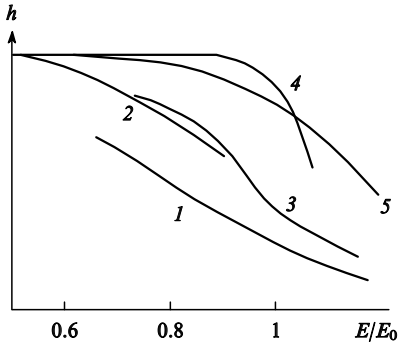


Figure 5. Dimensionless DF with respect to total vibrational energy E obtained from the PDF (Fig. 4): (*1*) NO_2; (*2*) CO_2; (*3*) SO_2; (*4*) CF_3I; (*5*) N_2O.

V. Fundamental microkinetic equation

For reactions occurring under thermal conditions and also for the majority of processes with laser excitation, the use of balance equations for the energy-averaged quantities is justified — for example in the case of the DF for species with respect to states having a fixed energy E between which repeated rapid transitions take place during the characteristic energy exchange time. When account is taken of the energy exchange processes, chemical reactions, and energy sources (sinks), the corresponding fundamental microkinetic equation assumes the form [4, 6, 7]

$$\frac{\mathrm{d}[\mathrm{A}(E)]}{\mathrm{d}t} = [\mathrm{M}]\int_0^\infty z(E')\mathrm{P}(E|E')[\mathrm{A}(E')]\mathrm{d}E' - \left[z(E)[\mathrm{M}] + \sum_i w_i(E)\right][\mathrm{A}(E)]\,. \tag{8}$$

Here $[\mathrm{A}(E)]$ and $[\mathrm{A}(E')]$ are the populations of the molecules A at the levels E and E' respectively, [M] is the overall concentration of species, $z(E)$ and $z(E')$ are the rate constants for the binary collisions when the energies of the molecule are E and E' respectively, $\mathrm{P}(E|E')$ is the probability of the transition of the kth species in unit time from the state with the energy E' to the state with the energy E [the kernel of the integrodifferential equation (8)], and $w_i(E)$ is the specific rate constant for the 'external' energy sources at the energy level E. The real distribution function $\mathrm{f}(E)$, which in the general case is different from the Boltzmann function as a consequence of the occurrence of the reaction, is defined by the relation

$$\mathrm{f}(E) = \frac{[\mathrm{A}(E)]}{\int_0^\infty [\mathrm{A}(E)]\mathrm{d}E}\,.$$

An important factor in the solution of the FME is the choice of a successful compromise between the physical justification of the model for the kernel of the integral equation $\mathrm{P}(E|E')$ and the 'mathematical convenience' in the solution of the FME with the selected kernel.

The most frequently employed characteristic of the energy exchange is the average portion of energy $\langle\Delta E\rangle$ transferred per collisions, which is linked to the kernel $\mathrm{P}(E|E')$ by the equation

$$\langle\Delta E(E)\rangle = \frac{\int_0^\infty (E'-E)\mathrm{P}(E'|E)\mathrm{d}E'}{\int_0^\infty \mathrm{P}(E'|E)\mathrm{d}E'}\,. \tag{9}$$

We shall examine the most widely employed functional representations of the kernel $\mathrm{P}(E|E')$.

1. Principal models for transition probabilities

a. Exponential model

Within the framework of the exponential model, the kernel assumes the form

$$\mathrm{P_d}(E'|E) = \exp\left(-\frac{E'-E}{\alpha_e}\right),\ 0 < E \leqslant E'\,.$$

Here the subscript d means that downward transitions on the energy scale are considered and α_e is a parameter characterising the 'half-width' of the kernel. The transition probabilities in the upward ($\mathrm{P_u}$) and downward ($\mathrm{P_d}$) collisions on the energy scale are linked by the detailed balance relation

$$\mathrm{P_u}(E|E') = \mathrm{P_d}(E|E')\frac{\rho(E')}{\rho(E)}\exp\left(-\frac{E-E'}{RT}\right),$$

where $\rho(E)$ and $\rho(E')$ are the densities of states for the internal energies of the molecule E and E' respectively; they are usually specified by the Whitten–Rabinovitch formula (7).[4, 7] The dependence of a_n on the energy in Eqn (7) may be neglected. For the ratio of densities, the following approximation is employed:

$$\frac{\rho(E')}{\rho(E)} = \exp[\mathrm{B}(E)(E'-E)]\,.$$

For a weak energy dependence of the parameter $\mathrm{B}(E)$, the integrals in Eqn (9) are expressed in a closed form.

b. Strong collisions

There are several equivalent definitions of the concept of 'strong collisions' (SC) itself (see, for example, Refs 2, 4 and 6). We shall deal with the following: strong collisions are those that in each collision between a molecule and the thermostat species, the equilibrium function is restored. In fact this is the zeroth approximation for the solution of Eqn (8), which makes it possible to reduce the latter to simple relations; it is then actually unnecessary to employ specific expressions for the kernel. Incidentally the latter assume the form

$$P(E|E') = \frac{\rho(E)}{Q}\exp\left(-\frac{E}{RT}\right).$$

Strong collisions as it were specify the upper limit to the rate of activation of the molecules and make it possible to introduce a specific scale for comparison with experimental data. The so called collision effectivenness is then introduced:

$$\beta_c = \frac{k_{d,0}}{k_{d,0}^{sc}},$$

where $k_{d,0}$ is the measured rate constant for unimolecular decomposition (or recombination) at the low pressure limit and $k_{d,0}^{sc}$ is the same quantity calculated in terms of the strong collision approximation. The analysis of experimental β_c data and also of the relation between β_c and $\langle\Delta E\rangle$ and the effective energy exchange cross-section σ_E may be found in a number of communications.[4, 6, 7, 14]

c. The statistical energy-exchange model

The statistical energy-exchange model for transition probabilities has a clear cut physical justification and is based on the assumption of a 'collision' complex between the excited molecule A and the thermostat species M during the existence of which a statistical mixing of the energy in the complex takes place. The specific form of the kernel is unduly cumbersome even when simplifying assumptions are made[6, 51] and we shall therefore not quote it. The statistical model has an upper limit to the portion of energy transferred.

The local-statistical activation model,[52] using the concept of the number of active oscillators participating in the energy exchange process during collisions, is a much improved version of the statistical model.[53–55] We may note that, within the framework of the local-statistical model, $\langle\Delta E\rangle$ depends on the parameters of a specific molecule and not only on the number of oscillators.

Another approach to the solution of the FME is based on the concept of the energy spectrum of highly excited molecules in the form of a set of discrete energy levels having the appropriate statistical weight and separated from one another by an amount equal to the average portion of energy transferred in the collisions. The stepwise excitation approximation makes it possible to formulate the so called step-ladder model.

d. The step-ladder model

In this model, transitions between neighbouring levels only are considered. The quantity $\langle\Delta E\rangle$ is the principal parameter varied. The system of kinetic equations, specifying the population of the energy levels, is formulated as follows:

$$\frac{d[A_i]}{dt} = \sum_j W(i,j) - \sum_i W(j,i) - \tag{10}$$

$$- \sum_i W(i) - \sum_j W_{E-V}(i),$$

where $[A_i]$ is the population of the energy level i, $W(i,j)$ and $W(j,i)$ are respectively the rates of activation and deactivation of the level i [the designation (i,j) will be understood as transition from the level j to the level i], $W(i)$ is the term taking into account the occurrence of bimolecular reactions and of spontaneous decomposition (for levels lying above the chemical reaction barriers), and $W_{E-V}(i)$ is the rate of transition between the ground and electronically excited terms (for molecules in which there is an 'inserted' electronically excited term).

Since transitions only between neighbouring levels are postulated, the sums in Eqn (10) consist of only two components:

$$\sum_i W(i,j) = k(i,j)[M][A_{i-1}] + k(i,j+1)[M][A_{i+1}],$$

where $k(i,j)$ is the rate constant for the activation of the level i on transition of the molecule from the level j.

The step-ladder model with allowance for chemical reactions and $E-V$ exchange has been examined in detail by Gaiduchenya *et al.*,[56] who give, in particular, the energy dependence of the rate constants in Eqn (10) and provide for the possibility of the independent variation of $\langle\Delta E\rangle$ for the ground and electronically excited terms. The authors[56] solved Eqns (10) by the numerical method proposed in Kalitkin's study.[57]

e. Bimodal exponential model

The bimodal exponential model may be regarded as the reasonable expansion of the simple exponential model in order to take into account explicitly the contribution of two types of collisions with transfer of large and small portions of energy.[58–61] Analytical relations between the principal parameters of the model have been obtained[62, 63] in a form analogous to that employed for the simple exponential model.

f. Stochastic modelling

The main advantage of the stochastic model is that it is free from *a priori* assumptions about the functional form of the kernel of the transition probabilities and can be applied with equal success to small and large polyatomic molecules and also to clusters.[64]

g. Weak collisions and the diffusion approximation

In the weak collision limit $\langle\Delta E\rangle/kT \ll 1$, the fundamental kinetic equation (8) is converted into the diffusion equation on the energy scale, for which exact solutions are known. This factor, in particular, has led to the fairly considerable popularity of this approximation. Troe and coworkers,[14] in whose studies the approximation apparently worked satisfactorily, also increased the number of adherents to the weak collision model.

2. Experimental data on the functional form of the kernel $P(E'|E)$

We may note that until recently the exponential model has been the most widely employed. The advantages of this model are its clarity, the possibility of obtaining a solution of the FME in an analytical form, and also the fact that the functional form of $P(E'|E)$ for certain polyatomic molecules is confirmed in broad outline by experimental facts. Direct confirmation of the adequacy of the exponential model has been obtained for the NO_2 molecule in experiments with molecular beams.[65] In these beams, one of the colliding partners is excited before collision by a laser into the energy region below the dissociation barrier. The probability of a collision jump to the dissociated state, the energy of which is higher than the given barrier, is well described by an exponential relation.

The data of Sanov *et al.*[65] 'face' the theory also with the more general question of the differentiation of the principal factors which permit the wide scale application of simple exponential relations for energy transitions in various relaxation processes: vibrational–vibrational ($V-V$), vibrational–rotational ($V-R$), and rotational–translational ($R-T$).

The question arises to what extent the above experimental data[65] may be interpreted within the framework of the more general biexponential model. The results of Sanov *et al.*[65] and the measurements of $\langle\Delta E\rangle$ based on the emission from NO_2 in shock waves are compared below.

The statistical and collision-statistical energy-exchange models are physically most justified. Other models are employed much more rarely. In most studies, it is emphasised that, in the description of the unimolecular decomposition rate constants (at least in the quasi-stationary approximation), the results of calculations are little sensitive to the functional form of the kernel [see Eqn (8)], but depend on the effective half-width of the kernel — $\langle\Delta E\rangle$. The situation for a nonstationary process is somewhat different. It has been shown[66] that the incubation characteristics of the decomposition of the N_2O molecule are described quite well

when an exponential kernel with parameters depending on the excitation energy is used.

The diversity of the forms of kernels employed makes it possible to estimate different aspects of the energy exchange processes with participation of HES and to identify the main ones among them when the results of the solution of the FME are compared with experimental data. A reasonable degree of specification of details in the description of the energy exchange involving HES, which is determined by the information content of the experiment, may be established in such a comparison.

Since the choice of a particular model is fairly arbitrary, it is essential to bear in mind certain fundamental limitations of each of them. Thus the statistical model clearly yields an upper limit to the transferred energies, while the step-ladder model fixes a portion of $\langle \Delta E \rangle$ fairly arbitrarily which sometimes requires additional analysis.

A multiplicity of publications have been devoted to the problem of the description of kinetic transformations with participation of HES on the basis of the solution of the FME. Almost all studies deal with the description with the aid of the FME of the results of measurements of the rate constants for chemical reactions with thermal, chemical, and optical activation.

A satisfactory agreement with experiment can be attained within the framework of different energy-exchange models, because the macroscopic rate constants are little sensitive to the level of specification of details in the description of the behaviour of excited states at a microscopic level. Formally this is associated with the fact that the macroscopic rate constant is determined as the result of the averaging of the microscopic rate constant $k(E)$ with respect to the distribution function:

$$k_{\text{macro}} = \int_{E_0}^{\infty} k(E) \mathrm{f}(E) \mathrm{d}E \,,$$

where $k(E)$ is the specific rate constant, which depends on the excitation energy E. Clearly, analysis of the directly observed characteristics of the functions $\mathrm{f}(E)$ can yield significantly more information about processes with participation of HES.

VI. Steady state distributions of the populations of highly excited states for unimolecular decomposition and bimolecular reactions

We shall consider the characteristic features of the DF in reactions behind shock waves. In the process involving the decomposition of molecules after rapid heating in the shock wave, it is possible to identify two stages — rapid (on thermal excitation in shock waves; its characteristic duration is $\sim 0.5-10$ μs; under the conditions of multiphoton laser IR excitation, the duration is $\sim 10^{-8}$ s), associated with activation processes before the HES chemical reactions barriers, and slow, due to the decomposition of the molecules proper. In the course of the second stage, the DF may be regarded as steady state in terms of energy levels. In this case, the right hand side of Eqn (8) is set equal to zero. It is easy to note that the form of the steady state DF depends only on the ratio of the rate constants for the chemical reaction and the deactivation process.

The CF_3I molecule proved to be one of the most convenient objects for the investigation of processes involving HES with an energy close to that of the barrier to unimolecular decomposition at the C–I bond. We shall specify two approaches to the interpretation of the results of absorption measurements. The first, developed by Dalidchik and coworkers,[34,45] is based on the use of 'hot' absorption bands in order to reconstruct the steady state HES distribution using the procedures described above for the transition from the partial distribution function with respect to the C–I bond to the distribution with respect to the total vibrational energy. The results are presented in Fig. 4.

In the second approach, examined by Abel and Herzog,[67] the changes in absorption in the 'hot' bands after the laser pulse excitation of the CF_3I molecule are recorded. The aim of the experiments of this kind was to find, by comparing the absorption at different wavelengths, the rate of the spontaneous decomposition of HES with an energy higher than that of the decomposition barrier and then to compare the results of the measurements with calculations based on the RRKM theory. The interpretation of the measurements is difficult owing to the presence of 'cold' and 'hot' ensembles of CF_3I molecules and the influence of collisions.

1. Triatomic molecules

In the study of triatomic molecules, the experiments were carried out with NO_2, N_2O, SO_2, CO_2 and O_3. The NO_2 and SO_2 molecules are particularly convenient for spectroscopic observations. Firstly, they have an excited electronic term 'inserted' in the ground state. The term is in quasi-equilibrium with high vibrational levels of the ground state. This makes it possible to carry out measurements based on both 'hot' absorption bands and on the emission in the UV and visible regions of the spectrum.[45,49]

Reliable results of measurements of the rate of relaxation at the lowest vibrational levels as a function of temperature and the collision partners as well as data on the relaxation of the HES make it possible to 'construct' a full picture of the energy exchange from the 'bottom' of the potential well to the states above the barrier, including $E-V$ transitions.

Secondly, bimolecular reactions with activation energies significantly lower than the decomposition barriers have been investigated for the NO_2 and SO_2 molecules. We may recall that the question of the role of the vibrational excitation of molecules in overcoming the bimolecular reaction barrier is still far from being solved. Analysis of the experimentally observed depletion of the distribution of the populations of the energy levels in the vicinity of the barriers to the bimolecular reactions

$$NO_2 + NO_2 \longrightarrow NO_3 + NO,$$

$$SO_2 + SO_2 \longrightarrow SO_3 + SO,$$

therefore yields data, which, when combined with the interpretation within the framework of the solution of the FME, may assist in significant progress towards the understanding of problems concerning the reactivity of highly excited molecules in collisions.

The attempts to find bimolecular exchange reactions occurring via a mechanism involving the subdivision of the process into the activation stage and the subsequent chemical stage proper have a long history, which does not lack certain dramatic features.[68]

$$AB + M \rightleftharpoons AB^* + M \,, \qquad \text{(I)}$$

$$AB^* + CD \rightleftharpoons AC + BD \,. \qquad \text{(II)}$$

Here AB and CD are molecular reactants, M is any of the species in the mixture, including an inert partner, and AB* is an active molecule which acquired a vibrational energy in stage (I) sufficient for chemical interaction with exchange of an atom or radical in the rearrangement process (II). The first model example

$$H_2 + D_2 = 2HD,$$

which was ineptly chosen [14] for experimental studies (because of its high sensitivity to the distorting influence of impurities), to a large extent compromised the idea of the activation mechanism of bimolecular reactions.

The activation mechanism of bimolecular reactions received the first experimental confirmation in relation to reactions involving nitrogen oxides.[69–71] The macroscopic manifestation of the state of nonequilibrium induced by the depletion of the populated states of AB* in reaction (II) has been discovered in the form of the dependences of the observed rate constant k_{obs} on the ratio of the reacting components and on the presence of an inert diluent. By analogy with the curves for unimolecular reactions, the corre-

sponding curves for bimolecular reactions were referred to as fall-off curves. The depletion, compared with the equilibrium distribution of the HES of the reacting SO_2 and NO_2 molecules, found with the aid of spectroscopic methods in shock waves (Fig. 5), directly confirms the activation mechanism of the exchange reactions. The distribution obtained is well correlated with the macroscopic dependences of k_{obs} on the mixture composition.

A detailed discussion of all the aspects associated with the macroscopic manifestations of the state of nonequilibrium in bimolecular reactions may be found in the communications of Zaslonko and Mukoseev.[69–71] We may note that the idea of the activation mechanism of bimolecular reactions and hence of the possibility of the manifestation of nonequilibrium effects has again begun to attract the attention of investigators in recent years.[72–74] However, the calculations are of a purely illustrative character.

2. Iron clusters

Vlasov *et al.*[75] observed nonequilibrium effects in the high-temperature decomposition of clusters in shock waves. In particular, such effects are indicated by the fact that the temperatures of the clusters T_c and of the surrounding gas T_g may differ greatly with $T_c < T_g$. The current level of development of the spectroscopy of clusters does not allow the probing of the distribution of the HES as in the case of molecular objects. However, it has been possible to demonstrate directly by spectroscopic methods the depletion of the HES distribution for iron clusters containing thousands of atoms.

VII. The energy-exchange mechanism and experimental data

1. Trajectory calculations

Trajectory calculations belong to the class of the most effective methods for the study of the dynamics of the HES energy exchange for polyatomic molecules in collisions. Until recently, these calculations were mainly illustrative in character for several reasons. Firstly as a rule, a trial potential is employed. Secondly, such calculations are technically difficult to carry out for a sufficiently large number of trajectories and there is no clear-cut criterion separating elastic and nonelastic collisions from which the completion of energy exchange might be inferred. Thirdly, the relation between the results of trajectory calculations and calculations within the framework of the FME is not clear. Fourthly, trajectory calculations performed with a specific pair of colliding partners and the possibility of transferring the relations established to other pairs of colliding molecules constitutes a separate problem.

Only recently has it become possible to overcome to some extent the majority of these difficulties. For example, the distribution of the probabilities $P(E|E')$ over the entire energy range from 0 to 100 kcal mol^{-1} has been found[59] with the aid of trajectory calculations for collisions of CS_2 with CO and was then used in the solution of the FME for the description of the relaxation of the initially excited molecules.

The systematic approach to the solution of the problem of the HES energy exchange must be regarded as the most productive and the qualitative features discovered[61,76,77] must therefore be specified.

1. The results of trajectory calculations for the transitions in the collisions of CS_2 with CO agree well with calculations employing the biexponential model for the probabilities of transitions subject to the condition that the exponents depend linearly on the energy.

2. The solution of the FME with a biexponential function for $P(E|E')$ agrees well with the trajectory calculations.

3. The calculations employing the simple exponential model with an energy-independent characteristic magnitude of the 'energy jump' agree poorly with the trajectory calculations, but the introduction of a linear dependence of this parameter on the energy alters the situation significantly. Calculations based on this 'improved' exponential model satisfactorily reproduce the characteristic features of the energy exchange.

4. Collisions which transfer of large portions of energy (strong collisions) make a much greater contribution to the overall energy exchange flux than the weak collisions. In other words, the contribution of the strong collisions to the average amount of energy transferred is the main one despite the fact that the fraction of such collisions is relatively small.

Trajectory calculations for small polyatomic molecules are used mainly to determine the ratio of the weak and strong collisions (in particular, the contributions of the $V-V$ and $V-R$ transitions).[59,76,77] For large molecules, such calculations demonstrate the importance of multiple 'chattering'§ collisions.[77,78]

Trajectory calculations make it possible to most fully discover the details of various mechanisms of the relaxation of the HES of polyatomic molecules in collisions. It is possible to identify four types of collisions with HES energy exchange.[79]

1. Direct single collisions of a buffer gas atom with an atom of the excited molecule lasting less than 300 fs. Thus $\sim 60\%$ of the nonelastic collisions of toluene molecules and an argon atom may be classified as direct and these constitute 50% of the energy exchange flux.

2. 'Chattering' collisions, the duration of which is greater than that of the direct collisions but is shorter than that required for the complete intramolecular redistribution of τ_{rel} (IVR). During the collision, the atom, as it were, executes several jumps from one site to another at the multidimensional atom–polyatomic molecule potential. Such collisions constitute $\sim 30\%$ of all the nonelastic collisions.

3. Collisions with formation of a complex the lifetime duration of which is greater than τ_{rel} (IVR). In such a complex, the energy is distributed statistically among all the vibrational modes and the RRKM theory is applicable to the calculations. The fraction of such collisions for toluene molecules and argon atoms is very small.

4. Supercollisions in which a very large amount of energy is transferred. However, their fraction is small, only $\sim 0.1\%$.

The first three types of collisions may be interpreted with the aid of the modified relaxation equation taking into account the vibrational energy balance. Furthermore, equations have been obtained for $\langle \Delta E \rangle$ in various limiting cases of the energy-exchange mechanisms and the independence of $\langle \Delta E \rangle$ of temperature has also been justified.[79]

One of the clearest mechanisms of the energy exchange of the HES of polyatomic molecules in collisions reduces to a sequence of $R-T$ transitions with subsequent rapid intramolecular mixing of the energy.[80] The characteristic quantity $\langle \Delta E \rangle$ for this mechanism amounts to $\sim RT$. The results of trajectory calculations for the collisions of SO_2 molecules and an Ar atom agree well with the results of calculations using the $V-R-T$ relaxation model. This means that the dynamics of the vibrational motion on the single collision time scale is insignificant for such calculations.

2. The influence of excited electronic terms in the HES reactions and energy exchange

In the course of the unimolecular decomposition and the reverse recombination process, species with unfilled electron shells frequently participate. Consequently one may expect the manifestation of fine structure effects. Several examples illustrating the possible scale of these effects have been examined.[81] The first example refers to the reaction

$$OH + O \longrightarrow H + O_2,$$

considered on the hypothesis that it proceeds within the limits of only one main potential energy surface. We then have

§ This term designates the ability of a monatomic collision partner to collide successively, several times, with several atoms of the excited polyatomic molecule.

$$k(T) = f_{el,0}(T)\, k_0(T)\,,$$

where $f_{el,0}(T) = g_{el,0}/Q_{el}(T)$ is the thermal population of the two lowest electronic states, leading to the formation of a complex, $g_{el,0}$ is the statistical weight of the state, $Q_{el}(T)$ is the combined partition function of the reactants, and $k_0(T)$ is the rate constant for the reaction between species in the lowest electronic states. Experiments have shown that the decrease in the thermal population of the lowest components of the fine electronic structure of the OH radical and the O atom with increase in temperature entails a decrease in the rate of reaction, because the highest components apparently do not contribute to the reaction. Consequently the above relation for $k(T)$ has been confirmed experimentally.

The second example concerns the reaction

$$OH + CO \rightleftharpoons HOCO^* \longrightarrow H + CO_2\,,$$

$$HOCO^* + M \longrightarrow HOCO + M,$$

for which the high pressure limit (k_∞) has been found experimentally. The reaction regime at low pressures (k_0) is well known. The first stage of the reaction is determined by capture, whilst in the second stage the reverse process — the decomposition of the active complex HOCO* — exerts an appreciable influence. If only the lowest components of the OH fine structure contribute to the reaction, then, by comparing the calculated and experimental rate constants, it is possible to find the expected contribution of the fine structure effect.

The possible influence of electronic terms on collision energy exchange processes has been tested in relation to the NO_2 molecule. The $^2B_2$ and $^2A_1$ states are known to be greatly mixed. Other electronic states, which are not linked optically, may be linked by collisions. The strong linkage between the $^2B_2$ and $^2A_1$ states promotes intramolecular exchange and, on laser excitation of molecules in the region of the dissociation barriers, the vibrational motion of the highly excited NO_2^* molecule is randomised. Apparently this in fact accounts for the absence of effects associated with the separate states for the spectrum of the products of the collision-induced dissociation.

The hypothesis of the important role of the electronic term in the NO_2 relaxation process is supported by the data of Toselli *et al.*[82] and Hartland *et al.*[83] In conformity with these data, the portion of energy transferred in collisions increases sharply starting with the levels corresponding to the location of the excited term. However, measurements in crossed beams did not demonstrate the influence of this term on the energy-exchange parameters.[65] The above contradiction can be resolved only on the basis of a more detailed description of the HES relaxation.

3. Reverse electronic relaxation. $V-E$ exchange

Molecules having an electronically excited term, the 'bottom' of which lies below the dissociation barrier, are favourable objects for the investigation of energy exchange. The electronically excited states of such molecules are as a rule found to be strongly linked to the vibrational levels of the ground state (Fig. 1). However, knowing the rate of energy exchange between these states, it is possible to infer how strong this linkage is.

In the collisionless regime, the mixing of the states (the Douglas effect) greatly lengthens the radiation lifetime, for example for NO_2^* it is more than 50 μs in the vicinity of the dissociation barrier. The long lifetime of molecules in the excited state (τ) is convenient for the 'transportation' of the excitation in the molecular beam.[65] For SO_2, this effect is most marked.

The phenomenon of the reverse electronic relaxation (RER) has been used in direct measurements of the time required for the establishment of the steady state association regime (t_{ss}) for the NO_2 and SO_2 molecules.[56, 84, 85] By varying the content of SO_2 in a mixture with argon, the total pressure, temperature, and the spectral range in the recording of emission, it has been possible to identify the component associated with the $V-E$ exchange processes in the overall time required for the attainment of the steady state dissociation regime.

The effectiveness of the RER has been estimated in relation to the resonance IR excitation process.[12, 88]

4. Vibrational relaxation of molecules in electronically excited states

The relaxation of vibrational energy within the limits of the electronically excited terms has been poorly investigated because the overall energy in these states is small and it is difficult to separate the vibrational relaxation process from the accompanying energy-exchange processes.

It has recently been possible to measure the vibrational relaxation times for the OH [89] and SO_2 [90] molecules with the aid of laser excitation and high-resolution LIF spectroscopy. The relaxation of diatomic molecules is somewhat outside the main topic, but the situation for SO_2 merits a comment.

The rate constant for the vibrational relaxation of SO_2 within the ground term at $T = 300$ K is 5×10^{-14} cm^3 s^{-1} (M = Ar).[91] On the other hand, the relaxation within the excited term is ~ 20 times faster,[90] *i.e.* the rate of relaxation is much higher than the rate of quenching of the fluorescence of the $^3B_1$ (0,1,0), $^3B_1$ (0,2,0), and $^3B_1$ (1,0,0) states of the SO_2 molecule. We may note that the fluorescence of the $^3B_1$ (0,0,0) state is quenched 20 times more slowly. Theoretical models for the description of experimental data have not yet been developed.

5. Dependences of the relaxation of the molecular highly excited states on temperature, collision partners, and the degree of excitation

The questions raised in the heading of the present section have been almost fully resolved in relation to the relaxation of the lowest vibrational levels of small molecules, which has been reflected in the literature (see, for example, Gordiets *et al.*[15]).

The situation is not quite so favourable as regards the HES of polyatomic molecules, particularly since it is necessary to take into account the vibrational degrees of freedom of not only the ground but also of the electronically excited terms.

We shall now turn to the energy dependence of the rate of relaxation of the HES. There are molecules for which it is possible to construct a complete relaxation pattern from the lowest vibrational levels up to the dissociation barrier. In the first place, this applies to the NO_2 molecule, characterised by exceptionally convenient spectroscopic features. For this reason, diverse methods have been tested on this molecule.

If one is dealing with a description in terms of the language of rate constants, then the problem formulated for triatomic molecules, (including NO_2) has been solved.[49, 51] The temperature dependences of three fundamental relaxation characteristics — the decomposition rate constant at the low pressure limit and the durations of the incubation phase and relaxation via the lowest levels — have been described in the above studies within the framework of a single approach based on the solution of the FME (Fig. 6).

As regards $\langle \Delta E \rangle$, the situation is more contradictory. According to the results of a number of studies,[69–71, 86, 87] the contribution of collisions with transfer of large portions of energy to the overall flux of activating collisions is notable (Table 1). Analysis of experimental data obtained in shock waves permits the following conclusions.

Firstly, in the lowest part of the energy scale the $V-T$ exchange proceeds with transfer of 600–2000 cm^{-1} vibrational quanta, depending on the temperature, with a probability from 10^{-2} to 10^{-3}.

Secondly, in the middle of the energy scale the portion of energy transferred $\langle \Delta E \rangle$ for NO_2 amounts to ~ 60 kJ mol^{-1} (Table 1), *i.e.* is equal to $\sim 4RT$ at $T \approx 2000$ K.

Thirdly, the activation mechanism of bimolecular reactions yields β_c for the highly excited states of the NO_2^* molecule with an energy close to the bimolecular reaction barrier.

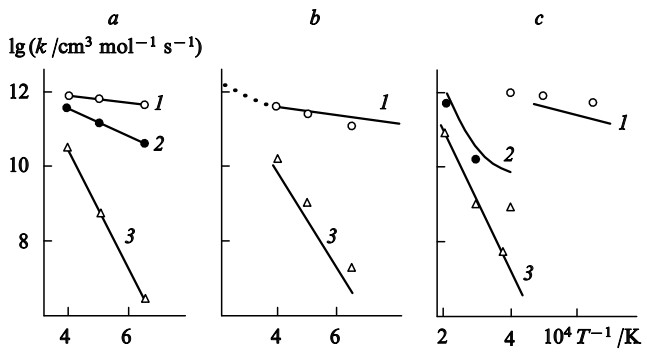


Figure 6. Experimental and calculated temperature dependences of the rate constants for various kinetic processes involving HES for the (*a*) NO_2, (*b*) N_2O, and (*c*) SO_2 molecules:[51] (*1*) relaxation rate constant; (*2*) incubation stage rate constant; (*3*) dissociation rate constant in the steady state regime; lines — fitting of experimental data in shock waves; symbols — results of the numerical solution of the FME.[51]

Fourthly, for transitions around the dissociation barrier there are independent β_c data in the range 0.1 – 0.01 (M = Ar, He, CO_2).[69]

In the two-channel model for the parallel occurrence of bimolecular and unimolecular reactions, $\langle\Delta E\rangle \simeq RT$ and $\sigma_E/\sigma_g = 0.1 - 0.01$ (see Refs 69 – 71 and the comments on these parameters in Refs 104 and 105).

Thus it has been possible to construct a self-consistent picture for the entire molecular vibrational energy scale on the basis of experiments employing the competing channels method and moderate-resolution emission-absorption spectroscopy.

The situation is different for data obtained by the high spectral resolution methods. Hartland *et al.*[83] found that the average portion of transferred energy for the NO_2 molecule is ~ 1300 cm^{-1}, *i.e.* equal to 10 RT at 300 K, which agrees with the results presented in Table 1 and is also supported by measurements of the rate of $V-T$ transitions.[91] However, the results of measurements in a beam[65] yield $\langle\Delta E\rangle_{up}$ in the range of only 110 – 310 cm^{-1}. Furthermore, this occurs for a relative energy of the collisions of the NO_2 molecules with Ar, He, O_2 and CO of $\sim 750 - 2400$ cm^{-1}.

What then is the problem? One of the causes of the discrepancies in the present author's view is the simplified interpretation of the experimental results. For instance, Puretskii[88] used for this purpose the simplest diffusion-type relaxation equation, which yields fairly good results for the upper energy scale but greatly distorts the results for relatively low excitation levels (according to the results of Zaslonko and Mukoseev,[87] in the region of the singular point).

One may postulate that the application of the exponential model for the transition probabilities will greatly improve the possibilities for the description of the primary data.[83] Even more interesting results may be obtained if the evolution of the DF with respect to total energy is reproduced on the basis of the observed transformation of the NO_2 high-resolution spectrum (antisymmetric vibrational spectrum). This function can then be interpreted on the basis of comparison with the solution of the nonstationary FME.

In relation to the conclusion that the activating collisions in experiments in molecular beams[65] obey the exponential model, one may assume that, for the present accuracy of the measurements, the experimental data may be fairly well described also by the biexponential model taking into account a certain hitherto unknown admixture of collisions with transfer of large portions of energy.

6. Characteristic features of the collision energy exchange of large molecules

The energy exchange in the collisions of complex molecules has been most fully investigated with the aid of the IR emission recording technique with laser pulse excitation (see the review of Barker and Toselli[18]).

Together with the properties characteristic of the HES of molecules with a small number of atoms, certain specific features are characteristic of polyatomic molecules.[18]

Firstly, the $V-R$ energy exchange is manifested in collisions with all partners apparently by virtue of the contribution of interactions over short distances. The model of such interactions is in essence close to the model of random multiple collisions.

Table 1. Results of the measurements of the average portion of transferred energy in collisions (ΔE) and of the ratio of the energy-exchange (σ_E) and gas-kinetic (σ_{gk}) cross-sections for the lowest energy of the term (E_0) in the range of observed energies ($\langle E\rangle$).

Molecule	Term	E_0 /kJ mol^{-1}	$\langle E\rangle$ /kJ mol^{-1}	ΔE /kJ mol^{-1}	T /K	σ_E/σ_{gk}	Excitation method
Emission measurements							
SO_2	$^1A_1$	0	360 – 422	39 ± 20	3600	0.01	Thermal
	$^1A_1$	0	360 – 422	39 ± 20	4150	0.01	"
	$^1A_1$	0	360 – 422	54 ± 22	2800	0.07	"
	$^1A_1$	0	380 – 518	30 ± 12	3600	0.02	"
	$^1B_1$	~ 334	138 – 263	92 ± 40	3000	0.003	"
	$^1B_1$	~ 334	138 – 263	84 ± 30	3300	0.004	"
	$^1A_2$	~ 334	138 – 184	87 ± 25	3300	0.001	"
	$^1A_2$	~ 334	25 – 138	88 ± 21	3300	0.01	"
	$^2B_1$	501	0 – 84	96 ± 25	3000	0.003	"
NO_2	$^2A_1$	0	42 – 167	58 ± 29	1800	0.02	"
	$^2B_1$	~ 150	84 – 167	$\geqslant 100$	1800	0.01	"
	$^2B_2$	~ 176	84 – 167	$\geqslant 63$	3600	0.01	Chemical [a]
Absorption measurements							
CO_2	$x\sum_g^+$	0	425 – 564	100 ± 45	2600	0.05	Thermal [b]
N_2O	$x^1\sum^+$	0	242 – 373	50 ± 23	1700	0.006	"
CS_2	$x^1\sum^+$	0	167 – 268	100 ± 31	1500	$\sim 10^{-3}$	Pulse laser [c]

[a] Chemical activation method — relaxation of the HES of the NO_2 molecules formed on recombination of NO and O. [b] Thermal activation method — relaxation of the HES after heating by the shock wave. [c] Treatment of the experimental data of Heymann *et al.*[105]

Secondly, the $V-V$ exchange occurs by virtue of the dipole–dipole interaction of the partners over large distances and the closeness to resonance between different vibrational modes is therefore significant.

Thirdly, the rate of the $V-R$ exchange increases in those cases where the molecules of the quenching gas have a permanent dipole moment, which may interact with the oscillating dipoles of the exciting molecule.

Fourthly, the presence of low-lying excited electronic terms may significantly accelerate the energy exchange.

The possibilities for the manifestation of different mechanisms of the $V-T/R$ and $V-V$ energy exchange have been examined in a study [18] based mainly on the results of mode-by-mode measurements of the induced IR emission by the molecules of CO_2 used as the 'quenching' gas in collisions with the excited molecules.

Gilbert and Zare [92] discussed the possible manifestation of quantum effects in energy exchange processes. The deactivation of the HES of azulene molecules in collisions with Ar and He was examined as an example. The appreciable difference between the effectiveness of ^{3}He and ^{4}He predicted in the above study was not confirmed experimentally.[18] In contrast to the azulene–argon system, the energy exchange in the azulene–helium system is poorly described by the method of trajectory calculations apparently because of the unsuccessful choice of the potential energy surface for the given pair.

7. The possible role of supercollisions in chemical kinetics

The question of the amount of energy transferred in collisions of excited polyatomic molecules with various partners has long interested kineticists. Owing to the lack of reliable data, the majority of their theoretical studies have been carried out in terms of the approximations of strong collisions (SC) or weak collisions (WC). The controversy concerning the question which of the mechanisms is more realistic has a correspondingly long history. In many respects, the majority of investigators have been inclined to assume the dominant role of WC under the influence of the studies by Troe and coworkers (see, for example, Refs 6 and 14).

This controversy became especially intense after the observation (experimentally and by a computational procedure [60]) of a significant fraction of collisions with transfer of large portions of energy. However, it had also been emphasised in earlier studies [69–71] that a whole series of multichannel reactions cannot be interpreted within the framework of the WC mechanism and that $\langle\Delta E\rangle$ is of the order of magnitude of RT. Since the effectiveness of the collisions β_c is much less than unity, *i.e.* the collisions can be in no way classified as purely 'strong', it became clear that it is more justified to apply the terms 'weak–strong' or 'strong–weak' collisions. Later the term 'supercollisions' (SUC) was introduced in the literature to designate the fact that in the overall energy exchange flux there is a fraction of collisions with transfer of large portions of energy.

We shall illustrate the possible role of SUC on kinetics by two examples. The first refers to the influence of SUC on the position and form of the transition curves for unimolecular decomposition reactions for a variable admixture of SUC in weak collisions.[60] Even when the fraction of SUC is 0.5%, their influence is considerable and exceeds the typical experimental errors. In view of the very common occurrence of decomposition and recombination 'transition regimes' in combustion processes and in atmospheric chemistry, much attention must be devoted to them.

The second example concerns multichannel transformations in atom-radical bimolecular reactions. The majority of such reactions occur with formation of a long-lived complex and are interpreted within the framework of the statistical theory of bimolecular reactions. The probability of a particular channel depends decisively on two parameters: the magnitude of the energy barrier for the corresponding channel and $\langle\Delta E\rangle$. In atom-radical reactions, one set of radicals is very often replaced by another set of radicals, which have different reactivities in chain reactions. This may intensify the sensitivity of the overall reaction to the type of a particular radical by a large factor.

Model calculations have been performed [93, 94] for two-channel decompositions within the framework of the exponential energy-exchange model. However, in the light of what has been said above about the possible role of SUC, it is necessary to investigate at least the 'sensitivity' of the recommended formulae to an admixture of SUC.

8. Energy exchange in collisions with clusters

The most detailed information about the energy exchange of clusters has been obtained on the basis of the method of trajectory calculations and also the molecular dynamics method.[95, 96] The cluster is usually modelled with the aid of the Morse pair potential and the Lennard–Jones pair interaction between clusters. The results of trajectory calculations for the energy exchange of specific clusters are naturally of independent interest. However, they are still more interesting as regards the applicability of different models to the energy exchange of macromolecules and clusters in collisions. We shall differentiate the following results among those obtained:

1) the energy exchange parameters depend on the structure of the cluster (for a fixed mass);

2) the energy exchange with clusters is more effective if the vibrational frequencies are reduced; the mass of the incoming atom and the relative velocities of the partners increase.

These results are fully consistent with the predictions based on Machan's pulse model,[97] according to which the $T-V$ transitions are accelerated as Massey's adiabaticity parameter diminishes. The relations found for the maximum energy transferred in a collision when the impact parameter is zero are useful for estimates.

$$\Delta E_{\max} = \frac{4 m_g m_a}{(m_g + m_a)^2} E_{rel} .$$

In the above relation m_g is the mass of the buffer gas atom and m_a is the mass of each of the atoms constituting the macromolecules m_M. The equation is most accurate for $m_a \ll m_M$ and $m_g \ll m_M$. On averaging over all possible orientations in collisions, the change in the internal energy of the cluster is

$$\langle\Delta E_{int}\rangle = \frac{\Delta E_{\max}}{2} .$$

If all other factors (*i.e.* E_{rel} and m_a) are kept constant, the energy transfer within the framework of the collision model increases with increase in m_g up to the maximum value $\langle\Delta E_{int}\rangle/E_{rel} = 0.5$ (E_{rel} is the relative translational energy of the colliding partners).

The above formulae are well supported by trajectory calculations for the collisions of Ar with Al_6 or with Al_{13}, *i.e.* $\langle\Delta E_{int}\rangle/\langle\Delta E_{rel}\rangle$ tends to 0.5 in the limit if the mass of the buffer gas atom is large, the vibrational frequencies are low, and Massey's adiabaticity parameter is small.

Estimates of $\langle\Delta E\rangle$ by the above formulae for collisions of iron clusters with an argon atom agree well with the value obtained in the theoretical description of the difference between the temperatures of the clusters and of the gas in thermal decomposition in shock waves.[98]

The details of the energy exchange mechanism in the collisions of clusters with inert gas atoms have been elucidated by comparing the results of trajectory calculations with the predictions of the ergodic collision model.[96]

We list below the features of such energy exchange closest to the subject of the present review.

The mechanism of energy exchange in the collisions of clusters depends on the intensity of the interaction and varies from the weak collision (WC) limit to the statistical strong collision (SC)

limit as the interaction energy varies from the scale of the van der Waals forces to values characteristic of a normal chemical bond.

For a weak interaction, the functional form of the transition probabilities in collisions $P(E|E')$ is well modelled by the relations of the partially ergodic collision theory. The functional form of $P(E|E')$ depends significantly on the parameter of the effectiveness of the collisional energy exchange β_E.

In collisions with strong interaction, a bimodal dependence of the transition probabilities $P(E|E')$ on the portion of transferred energy is observed. The central peak on this relation corresponds to weak collisions, whilst the 'wings' take into account the contribution of strong collisions.

VIII. Nonstationary distributions of the populations of highly excited states

1. The incubation phase of unimolecular decomposition reactions and the activation limit of bimolecular reactions

In the classical mechanism of a unimolecular reaction, the activation process is considered as the first stage, being followed by the chemical dissociation process proper or a rearrangement of the bonds in the activated molecule having an energy higher than the barrier to the corresponding process. For simplicity, we shall confine the treatment to the two commonest types of activation — thermal in collisions and optical in multiphoton excitation by IR irradiation (Fig. 1). Both types of activation are an example of activation 'from below'. The overall rate of the process is low up to the instant when the population of the active states of the molecules attains a steady state (not necessarily equilibrium) level. In such activation, it is necessary to pass through the entire 'ladder' of vibrational states before the barrier. In the majority of studies, the duration of this process is referred to as the incubation period and the latter is as a rule short compared with the main reaction time for an established steady state distribution function. It is more correct to call this time interval the relaxation time of the distribution function. For thermal reactions, these times approach one another with increase in temperature and conditions may be realised where the entire decomposition phase takes place as a nonstationary process and the population is small for most of the distribution function (including the region in the vicinity of the maximum). In such situations, the subdivision into incubation and steady state phases is no longer legitimate.

Naturally, the results of the measurement of the duration of the incubation phase τ_{inc} in the studies of unimolecular decomposition carry important information about energy exchange processes over the entire energy scale (from below up to the barrier). The measurement of τ_{inc} for unimolecular decomposition in shock waves is a difficult task. This problem has been solved sufficiently fully (with application of the emission technique for the excited electronic terms) only for triatomic molecules.[45, 49]

The results obtained were interpreted within the framework of the solution of the FME with reference to experimental relaxation data for the lowest vibrational levels (Fig. 6).

The theoretical calculations for the incubation phase in a collisionless dissociation process induced by resonance IR radiation have been carried out by Troe.[99] The durations of the incubation and steady state phases for this process are comparable and, if no account is taken of this fact, misunderstandings may arise when the results obtained by different workers for the rate constants and the product yields are compared. Comparison with the results of measurements of macroscopic rate constants is valid only when the form of the distribution function with respect to the internal energy of the reactants is the same!

Despite the fact that the duration τ_{inc} is in essence a characteristic of an integral process, the interpretation of the τ_{inc} yielded interesting results for the energy dependence, the rate of relaxation as a function of the degree of vibrational excitation of the molecule.[66]

A detailed analysis of studies on the incubation characteristics τ_{inc} of unimolecular decomposition reactions with thermal activation in the gas and as a result of collisions on the wall has been carried out.[50] In particular, the deficiencies of the calculations of τ_{inc} within the framework of the simplest exponential model with energy independent energy exchange parameters have been noted. These deficiencies have been overcome in other studies.[49, 51]

2. Transformation of the distribution of highly excited states

The modelling of kinetic processes involving HES has shown that measurements of only the integral parameters of the relaxation processes in chemical reactions and also of the steady state distribution functions are insufficient for the elucidation of the detailed mechanism of the energy exchange and reactions of highly excited molecules. The problem of the diagnostics of nonstationary distribution functions and of securing information about kinetic parameters involving highly excited molecules at a microscopic level therefore arises. Owing to the limited possibilities of the recording apparatus and a lack of satisfactory theoretical models, there has been little development of this field of study hitherto.

Detailed information about the energy-exchange processes can be obtained by creating a significantly nonequilibrium initial situation and by observing the subsequent transformation of the distribution function for a polyatomic molecule as a result of collisions with thermostat species. In this case, the average energy of the polyatomic molecules should differ greatly from the average energy of the thermostat species. Such situations occur in the laser excitation of molecules (the molecules are 'cooled' in the collision process) and also on thermal excitation of the molecules in shock waves (the molecules are 'heated' as a result of collisions).

There have been fairly numerous communications whose authors investigated the transformation of the initial distribution functions having a sharp maximum in the region of high energies. Such a 'narrow' distribution is generated as a result of chemical or optical pumping. The method employing intramolecular conversion, accompanying the absorption of a laser photon in the UV or visible region of the spectrum (Fig. 7), has come to be most widely used for the generation of 'narrow' HES distributions. The advantages of this method have been clearly demonstrated in

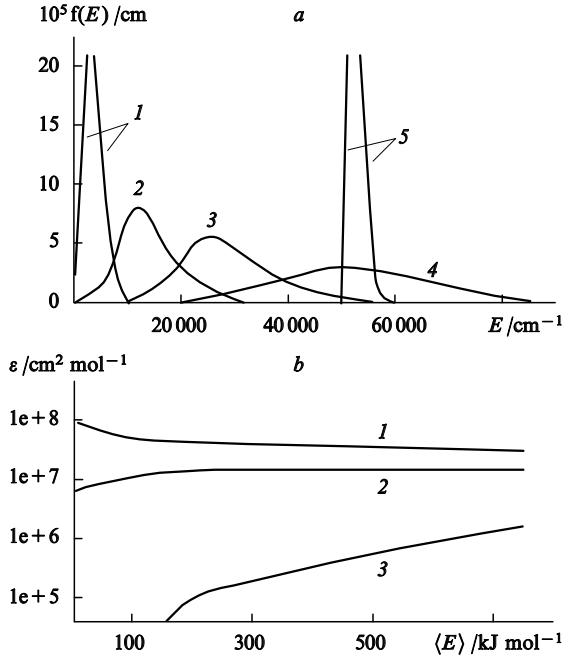


Figure 7. Transformation of the population distribution function on laser pulse excitation (*a*) and the dependence of the absorption coefficient of cycloheptatriene molecules on the wavelength and excitation energy $\langle E \rangle$ (*b*):[14] *a*: T/K: (*1*) 600; (*2*) 1200; (*3*) 1800; (*4*) 2800; (*5*) 300; *b*: λ/nm: (*1*) 180; (*2*) 200; (*3*) 250.

relation to a family of substituted cycloheptatrienes, CS_2, SO_2, $CrOCl_2$, azulene, *etc.*[100–104] The primary absorption step with subsequent rapid intramolecular conversion makes it possible to generate a microcanonical HES distribution within the limits of the ground electronic state. The electronic transition in the UV region is due to the optically active vibration of the polyatomic molecule, while the remaining vibrational modes play the role of an intramolecular thermostat. The vibrational energy at the $E_{\text{int}} \simeq \hbar\nu$ level becomes stochastic in a picosecond time interval. A significant advantage of this method is a clear-cut energetic definition of the initially generated distribution of molecules with respect to the total energy.

It has been concluded [14] that the relaxation of the average energy of the molecules may be described by the simple equation

$$-\frac{\mathrm{d}\langle E(t)\rangle}{\mathrm{d}t} \simeq z(\langle E\rangle)\langle \Delta E(E)\rangle , \tag{11}$$

where $z(\langle E\rangle)$ is the number of collisions of a 'hot molecule' having an energy $\langle E\rangle$ with the thermostat species. This relation is of the usual kind and has been used to interpret the primary experimental data for the relaxation of HES with UV laser excitation of the molecules. In order to be able to apply this relaxation equation, it is necessary to measure the average energy $\langle E\rangle$ of the molecule. This can be done by employing UV absorption spectroscopic,[48,49] IR fluorescence, and IR absorption [12,13] methods. Almost all investigators calibrate the measuring absorption channel if the distribution function with respect to the internal energy is known; for example, in terms of the empirical experimental dependence of the absorption cross-section of the molecule on the average store of the total energy ($\langle E\rangle$) (Fig. 7). The spectra of polyatomic molecules under equilibrium conditions (a canonical distribution of the molecules with respect to internal energy) and with UV laser excitation (a microcanonical distribution) are virtually the same, provided that the average energies of these ensembles are identical.[14] For the triatomic SO_2 and CS_2 molecules, the calibration is less satisfactory.[105]

The possibility of selecting a suitable wavelength in the UV absorption spectrum, for which an unambiguous relation between the absorption cross-section $\sigma(t)$ and the average energy of the molecules holds, has been justified.[67,103,104] Subsequently the kinetic absorption curve is transformed with the aid of the $\sigma(\langle E\rangle)$ relation into the $\langle E\rangle(t)$ relation, which is in fact used in Eqn (11). The cross-section of the deactivation process is then assumed equal to the gas-kinetic cross-section. As a result, the values of $\langle E\rangle$ for collisions with inert monatomic gases in the region of $(0.01-0.001)\ RT$ are obtained for CS_2 and SO_2 in the lower part of the potential well, which is frequently even less than the energy of the rotational quanta of the molecule. This agrees poorly with the overall picture of the vibrational relaxation of polyatomic molecules.

The above conclusions are a consequence of the limited applicability of the initial postulates underlying the interpretation of the experimental data. Firstly, analysis of the fundamental kinetic equation, carried out by Zaslonko and Mukoseev,[87] showed that Eqn (11) has a limited applicability. It is valid only for systems without vibrational energy sources or sinks as a result of the occurrence of chemical reactions of the HES and also for excitation energies significantly higher than the level of the average thermal energy of the thermostat molecules and subject to the condition that $\langle \Delta E\rangle \ll E$. In particular, neglect of this important factor (see Nikitin [14] and the literature quoted therein) led to a strong dependence of $\langle \Delta E\rangle$ on the excitation energy (or, what amounts to the same thing in the context of the above study, a strong temperature dependence of $\langle \Delta E\rangle$).

Secondly, the dependence of the absorption cross-section on the average energy of the molecules is not universal and for certain wavelengths may depend on the form of the distribution function and hence on the external conditions governing the activation of molecules.

3. Wave characteristics of the transformation of the distribution of populations on pulse excitation

We shall now consider the results of the analysis of the properties of the system of microkinetic equations for the population of the highly excited states of polyatomic molecules with pulse excitation. A generalised FME has been obtained [86,87] for the dimensionless distribution function of the populations in the presence of sources and sinks of excited states. With the aid of this equation, it is possible to find the correct limiting transitions to special cases of activation in the diffusion approximation and via the strong collision mechanism.

A fundamental feature of the analysis is the identification of singular points of the kinetic system, described within the framework of the FME, separating different dynamic energy-exchange process regimes. Depending on the energy function of the activation cross-section in collisions, the singular point is determined either by the average energy transferred in the collision $\langle \Delta E\rangle$ or by the average thermal energy of the species in the ensemble sRT, where s is the number of oscillators in the molecule. In the vicinity of the singular point, the energy-exchange kinetics can be satisfactorily described by a diffusion mechanism. Under conditions far from the singular points in the region of energies $E > \max\{\langle \Delta E\rangle, sRT\}$, the solution of the generalised FME is expressed in the form of a population travelling wave. The clearest results are obtained when the method of characteristics is employed. In the coordinate system linked to the moving population front, the solution has an exponential form with a characteristic region of the population gradient, which depends on $\langle \Delta E\rangle$. Under conditions far from the sources and sinks of the excited states and also for $E \gg \langle \Delta E\rangle$, the rate of movement of the population front is constant and only then can be fitted by the simple equation

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \langle \Delta E\rangle k_i^{(+,-)} ,$$

where $k_i^{(+,-)}$ are the rate constants for activation or deactivation and the 'plus' or 'minus' sign denotes the direction of motion of the population front, which depends on the initial conditions. In the absence of an energy dependence of $\langle \Delta E\rangle$ and $k_i^{(+,-)}$ the movement of the population front is of the automodel type: its form is retained and there is no dispersion in the distribution. When the population front approaches the barrier to the spontaneous decomposition of the excited molecules, the wave is retarded (there is a dispersion in the distribution) (Fig. 8).[87]

The above analysis provided a basis for a new method whereby the parameters of the energy exchange of highly excited states of polyatomic molecules may be determined experimentally. Its essential feature reduces to the measurement of the phase and amplitude characteristics of the relaxation process and the determination of the form of the population distributions. In the simplest formulation, for the solution of the problem it is sufficient to measure simultaneously the rates of change of the absorption (emission) at two wavelengths corresponding to two energy levels of the excited states. The simplest and at the same time fairly informative parameters of the experimental kinetic curves are the induction phase related to the time of arrival of the population front at the given energy level (τ_1 and τ_2 in Fig. 9) and the rate constant for the population of the given level ($\langle \Delta E\rangle$ characterises the form of the distribution of populations and $k_i^{(+,-)}$ characterises the amplitude of the populations in the given instant).

Two methods for the spectroscopic recording of the wave characteristics of the HES relaxation in shock waves have been applied. The first involves the recording of the emission from triatomic molecules in the UV and visible regions of the spectrum. The high sensitivity and a time resolution which is record-breaking for the shock wave technique have been achieved as a result of a spatially integrated emission system along the axis of the shock wave tube. The second procedure involves the recording of the 'hot' absorption bands of the molecules. An important precondi-

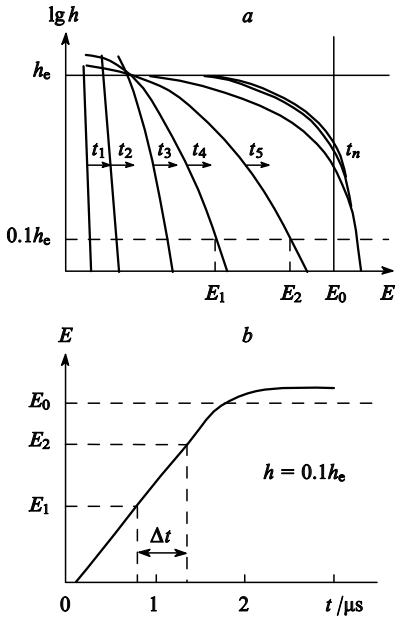


Figure 8. Examples of the numerical solution of the FME for the time evolution of the dimensionless DF, $h(E) = f(E)/f_{eq}(E)$, for vibrational energy on thermal activation in the shock wave; h_e — level of equilibrium population; E_0 — decomposition barrier; E_1 and E_2 — recorded energy levels; Δt — the time taken to traverse the population level over the specified energy range. *a*: form of DF at different times fitted by the relation $h(E) \simeq e^{-\alpha E}$, where $\alpha \simeq 1/\langle\Delta E\rangle$; $\Delta h(E)/[h(E)(E_2 - E_1)] = 1/\langle\Delta E\rangle$; *b*: trajectory of the motion in time of the constant-population level 0.1 h_e fitted by the equation $dE/dt = \langle\Delta E\rangle\ k_{rel}[M]$, where $(E_2 - E_1)/\Delta t = \langle\Delta E\rangle k_{rel}[M]$ and k_{rel} is the relaxation rate constant.

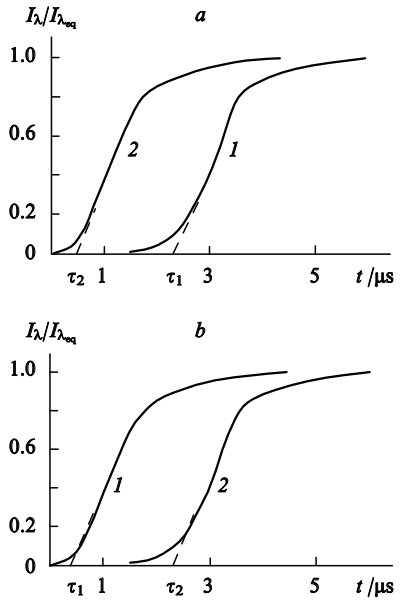


Figure 9. 'Distance traversed' by the population wave in the range of energies of NO_2 molecules of 212–240 kJ mol^{-1} (emission in shock waves): (*a*) relaxation 'from above' in the recombination process $O + NO \rightarrow NO_2^*$; (*b*): relaxation 'from below' in the collisions $NO_2 + Ar \rightarrow NO_2^* + Ar$; λ(nm): (*1*) 585; (*2*) 500; E(kJ mol^{-1}): (*1*) 210; (*2*) 240.

tion for the quantitative measurements is the possibility of calibrating the emission and absorption recording channels with respect to wavelength.

The measurements were performed with SO_2, NO_2, and CO_2 molecules.[86,87] The temperature range of the measurements was 1800–4000 K, the pressure was 2–5 atm, the diluent gas was argon, and the fraction of the molecular component was from 0.5% to 20%. The range of vibrational excitation energies capable of being recorded amounted to 10–130 kJ mol^{-1} for the absorption method and 180–500 kJ mol^{-1} for the emission method. In all the experiments, measurements were made simultaneously at at least two wavelengths. The energy gap between the energies of the recorded excited states was as a rule 30 kJ mol^{-1}.

The selected recording scheme made it possible to determine accurately the distance traversed by the population wave for the specified energy interval (Fig. 9). Opposite directions of wave travel were observed for NO_2 molecules with shock wave heating (relaxation 'from below') and in the recombination reaction $O + NO \rightarrow NO_2$ (relaxation 'from above'). The phase shifts of the signals in the two-channel recording, caused by the difference between the induction periods τ_1 and τ_2 were in the range 0.3–6 μs, while the rate constants for the population of the highly excited states in collisions were in the range $3 \times 10^{10} - 4 \times 10^{12}$ cm^3 mol^{-1} s^{-1} (in an argon atmosphere). The recording of the propagation of the population waves permits the direct determination of an important energy exchange parameter — $\langle\Delta E\rangle$. The clearest estimate of $\langle\Delta E\rangle$ is obtained from the law governing the motion of the population front:

$$\frac{E_1 - E_2}{\tau} = \langle\Delta E\rangle k_i^{(+,-)} ,$$

where E_1 and E_2 are the energy levels of the recorded excited states. We emphasise that this approach to the determination of $\langle\Delta E\rangle$ does not employ any additional (as a rule arbitrary) hypotheses concerning the energy-exchange mechanism.

The interpretation of the emission and absorption data in shock waves made it possible to determine the quantity $\langle\Delta E\rangle$ for the SO_2 and NO_2 molecules in the ground and excited electronic states and also for the CO_2, N_2O and CS_2 molecules in the ground states, which in all cases proved to be appreciably greater than RT, while the effective energy exchange cross-section σ_E is significantly smaller than the gas-kinetic cross-section σ_{gk} (Table 1). This result is of fundamental importance, because it provides a reliable basis for the elucidation of the real mechanism of the activation of polyatomic molecules in collisions without being restricted, as has been the usual practice hitherto in the vast majority of studies, to an arbitrary choice between two limiting mechanisms — strong collisions and the diffusional approximation. Unfortunately in the earlier determinations of $\langle\Delta E\rangle$ published previously the form of the distribution of populations during the relaxation of highly excited molecules was not monitored and in the interpretation of experimental data the authors introduced the seemingly obvious but in essence arbitrary assumption that $\sigma_E = \sigma_{gk}$.[14] The results of a number of investigations [69–71,86,87] have shown that the single-channel spectroscopic methods for the recording of the relaxation of highly excited molecules make it possible to determine only the product $\langle\Delta E\rangle\sigma_E$. For the separate determination of the multipliers, two-channel measurements with monitoring of the form of the distribution of the populations during relaxation are necessary. We may note that the spectroscopic recording of the steady state distribution of the populations of the HES of the molecules in the course of thermal decomposition behind shock waves, achieved earlier by Zaslonko and coworkers,[45,106] also makes it possible to determine only the product $\langle\Delta E\rangle\sigma_E$.

The recording of the nonstationary distributions of the populations of the HES of molecules during relaxation is free from the disadvantages noted above and permits the separate determination of $\langle\Delta E\rangle$ and σ_E. Evidently the application of high-resolution spectroscopy is promising for the monitoring of the distribution function in the course of the relaxation of the HES in collisions. This has been most strikingly demonstrated in relation to the NO_2 molecule: a Fourier spectrometer was used for the recording of the IR emission spectrum of NO_2 molecules excited by a laser in the range 800–10 000 cm^{-1} with a spectral reso-

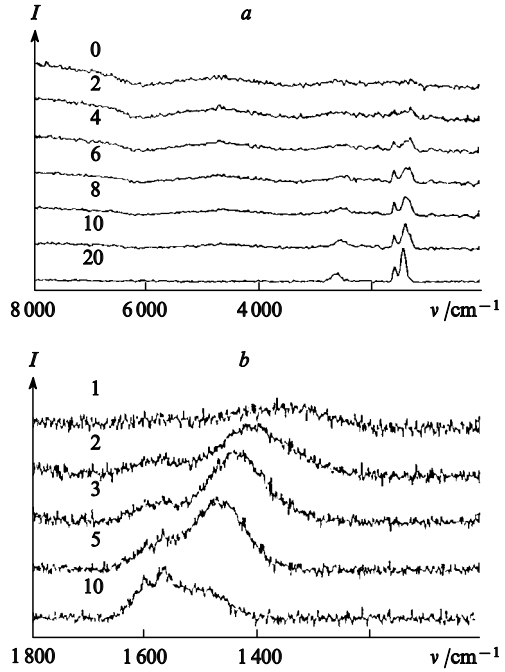


Figure 10. Transformation of the emission spectrum of the NO_2 molecule after excitation by a pulse laser.[83] Recording by the time-resolved Fourier transformation method. Resolution 1 cm^{-1}; NO_2 pressure 1.7 Torr. The numerals against the spectra represent the time interval (μs) after the laser pulse up to the start of the measurement.

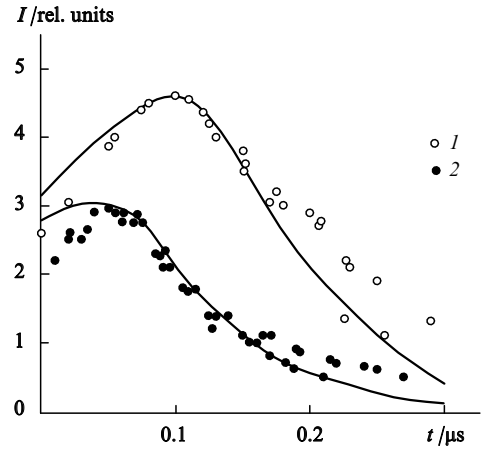


Figure 11. Time dependence of the absorption of light in the regions of $\lambda = 240$ nm (*1*) and 260 nm (*2*) by CS_2 molecules on pulse excitation by an excimer laser with an emission wavelength of 316 nm at $T = 1500$ K. Circles — experiment;[105] lines — calculation based on the model developed by Zaslonko and Mukoseev;[87] agreement with experiment at $\langle \Delta E \rangle = 100$ kJ mol^{-1}; $k_{rel} = 3 \times 10^7$ s^{-1}.

lution of 1 cm^{-1} and a time resolution of 0.5 μs.[83] These are indeed excellent apparatus parameters and they led to impressive results. It was possible to measure the energy dependence of $\langle \Delta E \rangle$ for the $NO_2^* - NO_2$ collisions (a sharp increase from $\langle \Delta E \rangle < 50$ cm^{-1} with $\langle E \rangle \simeq 13\,000$ cm^{-1} up to $\langle \Delta E \rangle \simeq 1300$ cm^{-1} with $\langle E \rangle \simeq 20\,000$ cm^{-1}) and a narrowing of the HES distribution as the relaxation process proceeds (Fig. 10).

In the initial instants of the relaxation, the NO_2 bands investigated (ν_3) have undergone a 'red' shift relative to the 'normal' frequency of 1617 cm^{-1} because the initial part of the emission signal is due to the emission from high levels with pronounced anharmonicity.

Unfortunately, no attempt was made [83] to relate the observed spectrum in the narrow frequency range to the total vibrational energy of the molecules and the simplest relaxation equation was used for the interpretation of the results of this study. We suggest that appreciably more information may be extracted from these data [83] on the basis of the description of the HES relaxation in the travelling population wave regime (see above).

This is well illustrated by the treatment of the primary experimental data on absorption in the 'hot' bands of the highly excited CS_2 molecules, such bands being generated on laser pulse excitation in the form of an initial δ-distribution (Figs 7 and 11).[103] If the shift of the absorption band observed in two-channel recording is ignored and they are treated by the single-channel method, as was done by Hippler *et al.*,[103] then the values of $\langle \Delta E \rangle$ obtained for the 'bottom' of the potential well are found to be very low. However, the observed shift of the absorption curves indicates the wave character of the propagation of the population wave. The values of $\langle \Delta E \rangle$ found agree well with the results for the SO_2, NO_2, CO_2, and N_2O molecules in shock waves (Table 1).

The average values of $\langle \Delta E \rangle$ and σ_E obtained by Zaslonko and Mukoseev [87] lead to the possibility of solving the problem of the reconstruction of the real functional form of the energy dependence of the transition probability $P(E|E')$ in collisions and also demonstrate the presence of an appreciable fraction of collisions involving transfer of large portions of energy. Recently, such collisions have attracted the attention of investigators, since their appreciable role in high-temperature chemical kinetics has been suggested.[60]

IX. Intramolecular relaxation

The problem of finding the characteristic rates of the intramolecular exchange of vibrational energy arose first in the interpretation of data on the kinetics of unimolecular reactions, vibrational predissociation, and the theory of mass spectra (see Refs 4 and 9 and the literature quoted therein).

Model ideas about the nature of the intramolecular relaxation (IVR) are used in all modern theories of elementary chemical reactions. The close relation between IVR and the chemical reaction step proper is illustrated by the energy diagram for the isomerisation process (Fig. 12). The quasi-harmonic description of the vibrations in the lower parts of the potential wells of the initial molecules and products becomes inapplicable on moving to the reaction barrier and at least one of the normal vibrations degenerates into translational motion along the reaction coordi-

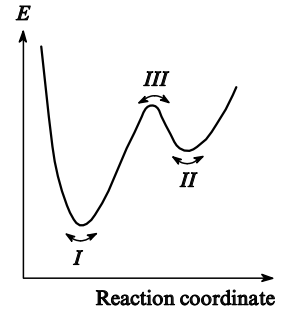


Figure 12. Energy diagram illustrating the transitions between various vibrational motion regimes in polyatomic molecules during the isomerisation process; $3n-6$ normal vibrations of the initial molecules in the region of the initial reactants (*I*) pass to the stochastic vibrational regime in the vicinity of the reaction barrier with degeneration of at least one vibration to translational motion along the reaction coordinate with subsequent generation of a new set of $3n-6$ normal vibrations in the region (*II*) of the reaction products; (*III*) transition region.[107]

nate [the vibrational frequency then becomes imaginary: $\omega = (k/\mu)^{1/2}$, $k < 0$].

The current state of studies on IVR has been described in a series of reviews (see, for example, Refs 107–109). Three dynamic IVR regimes, corresponding to different levels of excitation on the potential energy diagram, are distinguished. For a low level of excitation, whereupon the IVR times are relatively long, the application of IR diagnostic methods with high spectral resolutions is especially effective. In the second more extensive intermediate range of vibrational excitation energies, the IVR kinetics are usually followed by spectroscopic methods involving high vibrational overtones and methods involving the generation of HES with the aid of stimulated emission and fluorescence spectroscopic recording. The third group of studies refers to the region of highly excited states above the thresholds of dissociation, isomerisation, *etc*. reactions.

We shall quote two examples of specific IVR results. The first illustrates the dependence of the IVR rates on the structure and/or density of the states. The measurements were performed by the IR spectroscopic method with high (0.0005 cm^{-1}) spectral resolution in relation to the C–H bond in hydrocarbon molecules cooled in an ultrasonic jet. The results for a family of R–C≡C–H molecules with different end groups are presented in Table 2.

It can be seen that the rate of IVR depends little on the nature of the substituent groups: it changes by not more than a factor of

Table 2. Characteristic IVR times for the family of substituted ethyne derivatives.[107]

Molecule	τ_{IVR} /ps	Density of vibrational spectrum /No. of states per cm^{-1}
$CH_2(OH)-C\equiv CH$	500	20
$HC\equiv CCH_2CH_3$	270	22
$(CH_3)_3CC\equiv CH$	200	490
gauche-$CH\equiv CC(CH_3)_2H$	240	2400
trans-$CH\equiv CC(CH_3)_2H$	440	2400
$(CD_3)_3CC\equiv CH$	40	2800
$(CF_3)_3CC\equiv CH$	60	10^{11}

two when the density of states varies by ~ 2 orders of magnitude. The decrease in τ_{IVR} by approximately an order of magnitude is observed only for fluoro-substituted derivatives when the density of the vibrational spectrum increases by seven orders of magnitude.

The second example refers to the competition between IVR and predissociation. An interesting scheme for observations of this phenomena has been used for weakly bound clusters where even the excitation of the ground state in the near IR yields an excitation energy which is higher than the bond strength. Fig. 13 presents the measured and calculated spectra of the ν_5 antisymmetric DF stretching vibration in the trimer $(DF)_3$ with hydrogen bonds.[110] The average band contour corresponds to a D_{3h} cyclic structure. Fine structure, corresponding to a much denser spectrum (a difference by three orders of magnitude) than expected for a rigid molecule at 10 K can also been seen. This spectrum corresponds to the DF vibration with ring modes in the presence of mixing of various structures as a result of IVR. Mixing of this kind ensures an excitation energy sufficient to dissociate one hydrogen bond in the ring and to form the entropically more favourable flexible linear isomer, the characteristic time of the transition being ~ 40 ps. The opening of the trimer ring, which also corresponds to the dissociation of hydrogen bonds, is 10–100 times faster than the predissociation in the DF dimer. Such a large

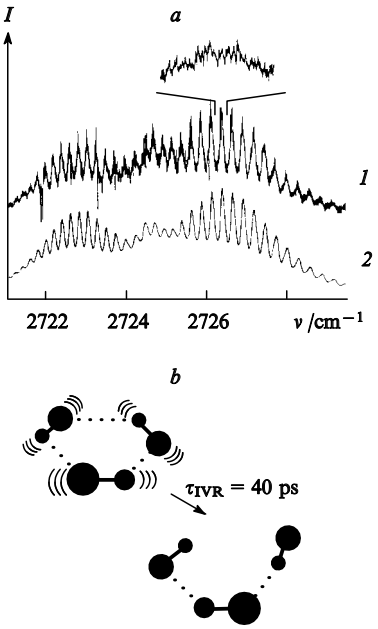


Figure 13. High-resolution IR spectrum in the region of the antisymmetric DF vibration in the $(DF)_3$ trimer formed on cooling in an ultrasonic jet to a temperature of 10 K (*a*) and schematic illustration of the transitions between two structures of the trimers with hydrogen bonds (*b*);[107] (*1*) experiment; (*2*) calculation.

difference between the rates may be associated with the influence of the strain in the ring structure on the dynamics of the dissociation of hydrogen bonds.

Interesting questions concerning the characteristic features of IVR in spaced out and dense spectra have been discussed in a number of communications (see, for example, Quack and Kutzelnigg [9]). The latest advances in the IVR theory have been described by User.[111]

1. The mechanisms of intramolecular relaxation and spectroscopic data

We shall examine the results of the study of the mechanisms and rates of IVR. The presence of heavy atoms in the molecule may induce a retardation of IVR.[112] This phenomenon may be interpreted both within the framework of simple models of molecules of the type XY_n with identical light atoms Y and a heavy central atom X [10] and within the framework of the model of local vibrational modes.[113, 114]

In another mechanism, leading to a higher rate of IVR, the linkage between vibrational modes via a series of lower-order resonances is considered.[115, 116]

One of the most important facts observed during the last decade is that there exists a fairly wide range of possible time scales for IVR with markedly different scales within the limits of one molecule [117, 118] and large differences for different types of chemical groups.[119, 120] The highly excited C–H vibrations in the alkyl and acetylenic groups may serve as a characteristic example. Vibrations have been investigated also by overtone vibrational spectroscopy for molecules ensuring a spectral resolution better than 0.1 cm^{-1} (Table 3).

The existence of internal rotations (such as those of methyl groups) also promotes a higher rate of IVR.[22, 121]

Table 3. Intramolecular IVR relaxation times for the initial excitation of the vibration of the CH group in alkanes and ethynes.[9]

Compound	τ_{IVR} /ps
Alkanes	
X_3CH (X = D, F, Cl, Br, CF_3)	< 0.1
XF_2CH (X = D, Cl, CF_3)	< 0.1
Ethynes	
$(CX_3)_3CCC{=}CH$ ($\upsilon = 1$) [a]	
X = F	$\geqslant 10-20$
X = H	> 200
X = D	$\geqslant 40$
$(CH_3)_3Si-C{\equiv}C-H$ ($\upsilon = 1$) [a]	$\geqslant 2000$
$CH_3CH_2C{\equiv}C-H$	> 269

[a] υ = number of vibrational level.

2. The rate of intramolecular relaxation as a function of the excitation energy

For the interpretation of kinetic data on the reactions of HES of polyatomic molecules, it is important to have sufficiently accurate and at the same time simple relations suitable for estimates of the rate of IVR. This problem has been solved [71] by employing the procedures of the theory of random functions. Relations were obtained for the estimation of the energy dependence of the time required for the vibrational motion to become stochastic, which agrees well with the results of trajectory calculations:

$$\tau_e\omega = (7-20)\frac{E_0}{\hbar\omega\upsilon^3},$$

(E_0 is the dissociation barrier, ω the average vibrational frequency, and υ the average number of vibrational states) and with the critical number of the average vibrational quantum υ_c for which the regular vibrational motion degenerates to random motion:

$$\upsilon_c = \left[\frac{64}{15}\frac{(s-1)!}{s^{s-1}}\frac{E_0}{\hbar\omega}\right]^{1/(s+2)}.$$

3. Unimolecular decomposition

The question arises whether unimolecular reactions, the kinetics of which should be interpreted outside the framework of the RRKM theory, can be observed. This question has for a long time troubled kineticists. The initial analysis of the problem was given in a communication [122] in which the most promising formulations of experiments for the observation of deviations from RRKM kinetics were noted.

The discovery of the collision-free dissociation of polyatomic molecules on resonance IR multiphoton laser excitation and the successful highly selective separation of isotopes naturally required an adequate theoretical interpretation and the discussion concerning the limits of applicability of the statistical theory of unimolecular reactions was therefore revived (see, for example, Refs 12, 13, and 16). It was found that, at least on the time scale of a $\sim 10^{-9}$ s pulse, the RRKM theory described quite satisfactorily the kinetics of the spontaneous decomposition of active polyatomic molecules excited by a pulse from an IR laser.

Simultaneously with the development of spectroscopic methods, attempts were made to seek molecules on which one can demonstrate the nonstatistical features of the spontaneous decomposition rate constants $k(E)$, but these were unsuccessful. The constant $k(E)$ depends decisively on the rate of IVR (see above).

We may also note a novel approach, proposed for the observation of kinetic phenomena, which goes beyond the framework of the traditional RRKM theory.[123] This concerns the mechanism of reversible unimolecular reactions and the possibility, in principle, of determining the equilibrium canonical rate constants at low pressures without resorting to a laborious measuring procedure and treatment of fall-off curves. It has been demonstrated on model examples using the solution of the FME that such paradoxical behaviour is realistic and methods for the corresponding observations have been noted. However, an experimental test of the ideas put forward by Quack [123] has not so far been carried out.

One of the latest attempts to discover deviations from the theory of unimolecular reactions on the decomposition time scale of the order of several microseconds has been made by Schlag and Levin.[124] The attempt to revise the statistical theory was stimulated by the apparently anomalously short decomposition times for large polyatomic molecules on excitation by electron impact in a mass spectrometer chamber. The authors used the classical version of the statistical theory but they introduced the hypothesis that for large polyatomic molecules the IVR process in the range of energies above the decomposition barrier does not ensure the complete mixing of the energy, as a result of which the number of effective oscillators s_{ef} is significantly smaller than the total number of oscillators $s = 3n - 6$. The large difference between s and s_{ef} is equivalent to an appreciable decrease in the lifetime of the active states of the large molecules. The question therefore arises to what extent the hypothesis that the IVR process may be so slow is valid. However, it was found that the above discrepancy between the observed and measured lifetimes of the active states of large molecules may be satisfactorily accounted for within the framework of a modified version of the statistical theory in which the vibrational temperature of the molecule has been taken into account and by calculating on this basis s_{ef} without resorting to the hypothesis that IVR is slow.[125]

X. Reactions of highly excited states of polyatomic molecules

1. Spontaneous unimolecular decomposition

The first successful attempts to measure the specific rate constants $k(E)$ for the spontaneous decomposition of polyatomic molecules with an energy greater than the barrier D involved photoactivation in stationary and pulse regimes.[6] In full conformity with the RRKM theory, the values of $k(E)$ found for the molecules of the cycloheptatriene family varied as the number of groups adjoining the main ring was altered (Fig. 14). The results of direct measurements of $k(E)$ in the decomposition of ions have been described.[7,8]

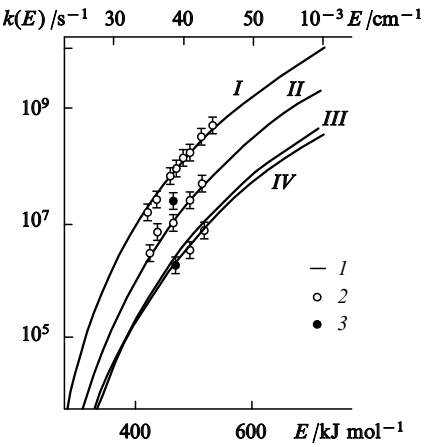
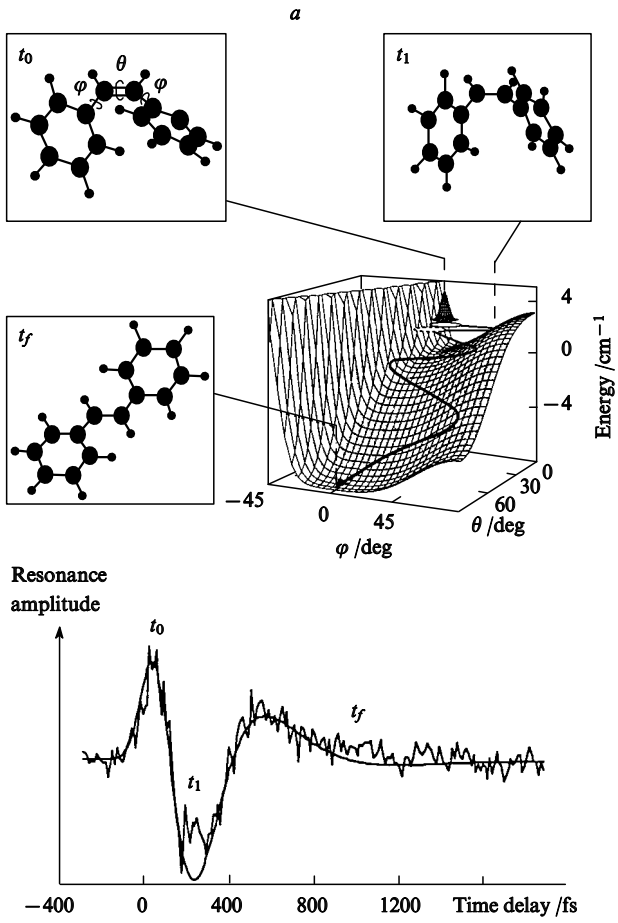


Figure 14. Energy dependence of the specific rate constants for the spontaneous decomposition of active molecules of cycloheptatriene (CHT) (*I*) and its methyl derivative (Me-CHT) (*II*) and ethyl derivative (Et-CHT) (*III*, *IV*): (*1*) determination from the rate constant for isomerisation $k_\infty(T)$ under thermal conditions at the high-pressure limit; (*2*) interpretation of the stationary photolysis on the basis of the Stern–Volmer curves; (*3*) laser pulse photolysis with recording of the evolution of the 'hot' absorption bands.[7]



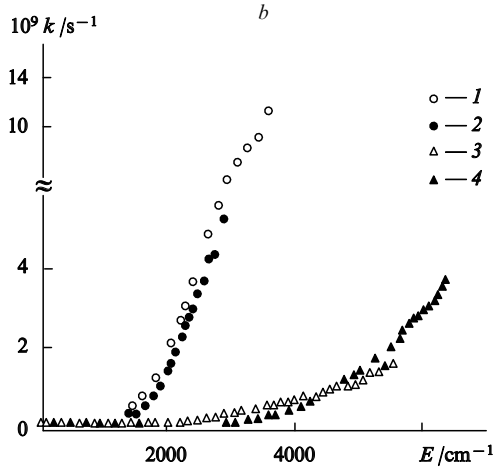
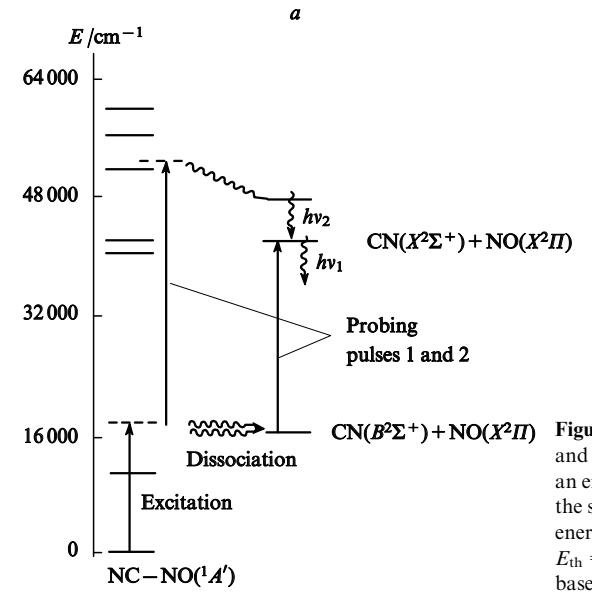


Figure 15. Femtosecond dynamics of the isomerisation of stilbene:[126] (*a*) transitions between different structures of stilbene and the trajectories of the motion of the representative point on the potential energy surface; (*b*) dependence of the rate constant for the spontaneous decomposition of stilbene (*1*), 4-methoxystilbene (*2*), 4,4′-dimethoxystilbene (*3*), and 2-phenylidenestilbene (*4*) on, the amount by which the vibrational energy exceeds the barrier.[127]

For direct measurements of $k(E)$ for reactions with neutral molecules, it is most effective to employ the following methods for the preparation of HES with a clearly defined energy state: single-photon excitation of high vibrational overtones within the limits of the ground electronic state; single-photon excitation of electronically excited states followed by rapid internal conversion to high vibrational levels of the ground state (Figs 1 and 7).

The methods based on the molecular 'hot band' spectroscopy proved entirely capable of ensuring the necessary level of sensitivity and time resolution for measurements of $k(E)$. Sufficiently 'broad' HES distributions are also obtained on multiphoton IR excitation.

The results of direct measurements of $k(E)$ by various methods have been published.[126, 127] The isomerisation reactions of stilbene (Fig. 15) and the spontaneous decomposition of NCNO molecules by ultrashort laser pulses (Fig. 16) have been examined. The manifestation of threshold effects for isomerisation and appre-



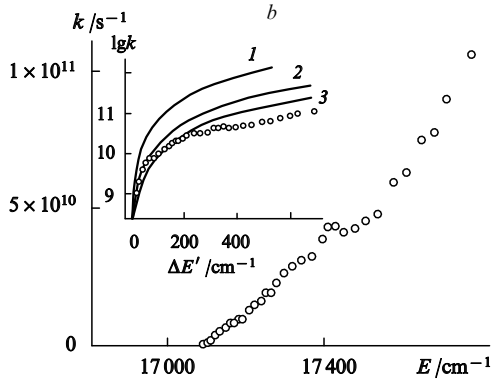


Figure 16. Energy diagram for the transitions on laser excitation of NCNO molecules and the spontaneous decomposition of NCNO* molecules excited by a laser pulse to an energy region above the spontaneous decomposition barrier (*a*) and dependence of the spontaneous decomposition rate constant on the amount by which the vibrational energy of the NCNO* molecules exceeds the decomposition barrier $E_{\rm th}$ = 17 083 cm^{-1} (*b*).[127] Results of theoretical calculations of $k(E)$: (*1*) calculation based on the canonical theory of the reaction phase space; (*2*) and (*3*) calculation using modified versions of the statistical theory; circles — experimental data.

ciable changes in the position of the barrier and in the rates of isomerisation as a function of structure can be seen in Fig. 15.

2. Bimolecular reactions of highly excited molecules

The characteristic features of bimolecular reactions of diatomic and polyatomic molecules with a moderately high vibrational excitation have been examined in several reviews (see, for example, Bauer [68] and Zewail [126]).

We are interested in bimolecular reactions of polyatomic molecules with a sufficiently high vibrational energy. The concept of the vibrational mode loses significance for such molecules and their reactivity depends primarily on the total vibrational excitation energy or, more precisely, on the distribution function with respect to the total vibrational energy.

Analysis of the activation characteristics of bimolecular reactions remains the first and so far the only systematic method for the kinetic determination of the specific rate constants for bimolecular reactions of the HES of polyatomic molecules.[69]

The principal idea underlying the activation mechanism is illustrated by the following Scheme 1.

Scheme 1

Unimolecular reactions	Bimolecular reactions
$A \longrightarrow$ products	$A + B \longrightarrow$ products
$A + M \underset{-a}{\overset{+a}{\rightleftharpoons}} A^* + M$	$A + M \underset{-a}{\overset{+a}{\rightleftharpoons}} A^{**} + M$
$A^* \xrightarrow{k(E)}$ products ($E \geqslant E_m$)	$A^{**} + B \xrightarrow{k_b(E)}$ products ($E \geqslant E_{bim}$)
$k_d = \frac{k(E)(k_{+a}/k_{-a})}{1 + (k(E)/k_{-a}M)}$	$k_{bim} = \frac{k_b(E)(k_{+a}/k_{-a})}{1 + (k_b(E)[B]/k_{-a}[M])}$
Limiting cases	
Equilibrium regime	
$[M] \longrightarrow \infty$	$\frac{k_b(E)}{k_{-a}}\xi_B \ll 1$
$k_{d,\infty} = \frac{k(E)k_{+a}}{k_{-a}}$	$k_{bim,\infty} = \frac{k_b(E)k_{+a}}{k_{-a}}$
Regime limited by activation	
$[M] \longrightarrow 0$	$\frac{k_b(E)}{k_{-a}}\xi_B \gg 1$
$k_{d,0} \simeq k_{+a}[M]$	$k_{bim,0} \simeq \frac{k_{+a}}{\xi_B}$

A* and A** are active molecules which have acquired in activating collisions an amount of energy greater than the barrier to the unimolecular (E_m) and bimolecular (E_{bim}) reactions respectively; ξ_B is the mole fraction of component B in the mixture.

The dependences of the observed bimolecular reaction rate constant on mixture composition can be conveniently referred to as transition curves by analogy with unimolecular reactions. We shall now formulate the relations which have been established on the basis of the interpretation of the fall-off curves for the rate constants for bimolecular reactions involving nitrogen oxides (Table 4).

1. The ratio $\overline{k}_b/k_{-a}$ is in the range 4–20. Here $\overline{k}_b$ is the rate constant for the bimolecular reaction averaged for the energies above the barrier E_{bim} and k_{-a} is the deactivation rate constant.

2. The constant k_b depends both on the store of vibrational energy and on the gas temperature. The translational barrier to the bimolecular reaction of the HES is $\sim 10\%$ of the overall barrier.

Table 4. Rate constants for bimolecular reactions (k_{bim}) and the effectiveness of collisions (β_c) for highly excited states of the NO_2* and N_2O molecules.

Reaction	$\overline{k}_b/Z_{gk}$ [a]	T/K	E_b /kcal mol^{-1}	$10^2\beta_c$ [b]
$N_2O^* + NO$	0.08	1680	41	0.4
$N_2O^* + CO$	0.06	1590	54	0.3
$NO_2^* + NO_2$	0.14	1670	39	0.3

Note. 1. The results for k_b and β_c were obtained on the basis of a theoretical description of the transition curves (Fig. 17). 2. The dependence of β_c on the excitation energy is fitted by the relation $\beta_c \simeq E^2$. 3. The dependence of k_b on the translational temperature T_g is fitted by the equation $k_b \simeq \exp(-E/RT)$, where E is the translational barrier to the reaction of the vibrationally excited molecule.

[a] $\overline{k}_b$ is the average value in the region $E > E_b$ (the bimolecular reaction barrier) and Z_{gk} is the frequency of the gas-kinetic collisions. [b] The value of β_c for the excitation energy in the vicinity of the barrier to the bimolecular reaction: $\beta_c \simeq \langle E \rangle^2$.

3. The observations for k_b have been interpreted on the basis of the collision-stochastic model, according to which during the period of the interaction of the reactants all the vibrational modes of the polyatomic molecules contribute to the reaction rate (we may note that this property is fully correlated with the multiple 'chattering' collisions mechanism).

4. The activation characteristics are observed only for reactions with a high barrier, *i.e.* their rates increase markedly at high temperatures.

The question arises why nonequilibrium effects involving depletion of the distribution function with respect to vibrational energy in the vicinity of the barrier are manifested precisely for reactions with fairly high barriers. This can be naturally attributed to the fact that, for reactions of polyatomic molecules with a sufficiently high level of excitation, the vibrational motion of the active molecules is nearly stochastic and the reactivity therefore increases as a consequence of the contribution of all the vibrational modes. Furthermore, the ratio k_b/k_{-a}, which determines the scale of the depletion of the distribution functions, increases with increase in temperature.

The distorting influence of bimolecular reactions of the HES of the NO_2 and SO_2 molecules on the form of the distribution function with respect to energy has been demonstrated.[49, 56] In

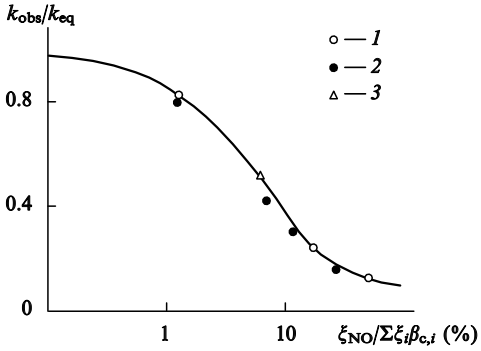


Figure 17. Transition curve for the rate constant for the exchange reaction $N_2O + NO \rightarrow N_2 + NO_2$: (*1*) 1% N_2O + 2% NO, 2.5% N_2O + 97.5% NO, Ar diluent; (*2*) recalculation of data in terms of inflammation limits; (*3*) 2.5% N_2O + 25% NO, CO_2 diluent. Data (*1*) and (*3*) were obtained in shock waves; ξ_i — mole fractions of the components; $\Sigma\xi_i\beta_{c,i}$ — the effectiveness of the partners $\beta_{c,i}$ in activating collisions averaged over the mixture; k_{obs} and k_{eq} — the observed rate constant for the bimolecular reaction and its equilibrium value respectively.

particular, this influence is fully correlated with the macroscopic manifestations of the state of nonequilibrium (Fig. 17).[69–71]

An interesting development of the idea concerning the role of internal excitation on the reactivities of the partners in bimolecular reactions has been put forward.[74] The high effectiveness of the reactions under conditions where the reactants are 'dissolved' in a cluster which undergoes impact heating can be explained by the fact that the internal degrees of freedom of one or both reactants are excited by the cluster.

3. Generalising concepts for the bimolecular reactions of highly excited polyatomic molecules

It appears at first sight that the family of bimolecular reactions is so diverse that it is difficult to speak of any kind of generalising concepts. Fortunately such is not the case and we shall in fact attempt to illustrate this.

The statistical theory of bimolecular reactions rightfully occupies the central place in the list of such concepts. The possibilities of this theory have been best demonstrated in Troe's review, which has been justifiably given the emotive title 'The Colourful World of Bimolecular Reactions'.[62]

Why is the rating of the statistical theory so high? There are two main reasons. Firstly, the wide occurrence of bimolecular reactions, proceeding via a stage involving the formation of a long-lived complex, has an effect; secondly the entire procedures of the RRKM theory are applicable to reactions of this kind, which creates the necessary preconditions for the development of an overall computational set up.

The second concept may be regarded as heuristic systematic treatment. Such systematic treatment is based on the subdivision of the activation barrier for the reaction into the contributions due to the vibrational and translational degrees of freedom and the significance of the coefficient of the utilisation of the vibrational energy in overcoming the barrier is assigned to the ratio of these contributions.[2, 3, 129]

The collision-stochastic model may be considered as the third concept.[71] Initially this concept was put forward to account for the high preexponential factors for the bimolecular exchange reaction rate constants (Table 5), after which experimental data confirming it were obtained also by laser activation of polyatomic molecules.

Table 5. The Arrhenius parameters for the rate constants for certain bimolecular exchange reactions of valence-saturated diatomic and triatomic molecules ($k = \mathrm{A}e^{-E/RT}$).

Reaction	$\lg A$ [a]	E [b]	T/K
$N_2O + CO \longrightarrow CO_2 + N_2$	16.0	53	1400–3000
$N_2O + NO \longrightarrow NO_2 + N_2$	15.2	48	1360–1890
$NO_2 + NO_2 \longrightarrow NO_3 + NO$	14.8	34	1400–2300
$NO_2 + CO \longrightarrow CO_2 + NO$	14.4	33	1400–2300
$SO_2 + SO_2 \longrightarrow SO_3 + SO$	15.0	70	3000–4000
$CO_2 + C^{18}O \longrightarrow C^{18}O_2 + CO$	16.33	66.7	3000–4000
$CO_2 + {}^{13}CO \longrightarrow {}^{13}CO_2 + CO$	13.94	48.9	3000–4000

[a] The dimensions of A are $cm^3\,mol^{-1}\,s^{-1}$. [b] The dimensions of E are kcal mol^{-1}.

If all the internal degrees of freedom contribute to the overcoming of the reaction barrier, then the equilibrium rate constant for bimolecular reactions k_{eq} is defined by the equation

$$k_{eq} = A_{eq}\exp\left(-\frac{E_0}{RT}\right) = \int_{E_0}^{\infty} k_b(E_V, E_RT)f_0(E_V, E_{RT})dE_V dE_{RT}\,. \tag{12}$$

Here A_{eq} is the pre-exponential factor, E_0 the activation energy for the equilibrium bimolecular reaction, $k_b(E_V, E_{RT})$ the rate constant for the bimolecular reaction as a function of the vibrational (E_V) and rotational-translational (E_{RT}) energy, and $f_0(E_V, E_{RT})$ the distribution function, proportional, in particular, to the density of the energy spectrum $\rho(E)$. The proportionality of k_{eq} to the total density of the spectrum $\rho(E)$ therefore follows from Eqn (12), which is in fact the reason for the high pre-exponential factors for the equilibrium bimolecular reaction rate constants.

If one is dealing with a detailed kinetic analysis of equilibrium rate constants for bimolecular reactions and hence for processes involving HES during the collision of the partners, then the simplest two-level mechanism must be supplemented by a more detailed consideration of processes involving excited molecules at the 'inlet' (initial reactions) and 'outlet' (reaction products). One of the versions of such consideration of the reaction

$$AB + C \longrightarrow P_1 + P_2\,,$$

where AB and C are polyatomic molecules and P_1 and P_2 are the products, is presented in the following scheme:

$$AB + M \underset{k_{-a}}{\overset{k_a(E)}{\rightleftarrows}} AB^*(E) + M\,,$$

$$AB^*(E) + C \xrightarrow{k_B(E,E_t)} [AB^*(E)\cdot C]\,,$$

$$[AB^*(E)\cdot C] \xrightarrow{k_r(E)} (ABC)^*\,,$$

$$(ABC)^* \longrightarrow \begin{cases} \xrightarrow{k(E)} (ABC)^{\neq} \xrightarrow{k^{\neq}} P_1 + P_2 \\ \xrightarrow{k'(E)} [AB^*(E')\cdot C] \xrightarrow{k_B^{\neq}} \\ \qquad\qquad \longrightarrow \quad AB^*(E') + C. \end{cases}$$

Here $AB^*(E)$ is a molecule with an internal energy E, which is sufficient for it to react, $k_a(E)$ is the rate constant for activation in the energy range $E + dE$, $[AB^*(E)\cdot C]$ is the collision complex in which the distribution of energy is determined by the initial distribution of the internal energy of the fragments before collision and the relative motion of AB* and C at the effective interaction potential, $k_B(E,E_t)$ is the rate constant for the 'capture' process indicated above, E_t is the energy of translational motion, $k_r(E)$ is the rate constant for the redistribution of energy in the collision complex, (ABC)* is the activated molecule in the traditional sense as understood in the RRKM theory, and $[AB^*(E')\cdot C]$ is the collision complex.

The flux of species through the configuration of the activated state is proportional to the partition function, so that the ratios of the vibrational-rotational partition functions of the collision complex (Q^*) and the activated molecule ($Q^{\#}$) must be compared in making a choice of the rate-limiting stage in the chain of transformations of the states involved in bimolecular reactions of active molecules. For the ratio of the vibrational-rotational partition functions, one may write

$$\frac{Q^*_{vr}}{Q^{\#}_{vr}} = \frac{Q^*_{rot}}{Q^{\#}_{rot}}\left(\frac{E_0}{RT}\right)^{(1/2)s_r^* + s_v^{\#}} \times \times \frac{E_0^{s_v^{\#} - s_v^*}F_E}{\Gamma[s_v^* + (1/2)s_r^* + 1]} \times \frac{\prod_i \hbar\nu_i^{\#}}{\prod_i \hbar\nu_i}\,, \tag{13}$$

where the * and # superscripts refer to the collision and activated complexes respectively, Q^*_{rot} and $Q^{\#}_{rot}$ are the rotational partition functions, s_v and s_r are the numbers of vibrational and rotational degrees of freedom, and F_E is a multiplier taking into account the energy dependence of the number of states of the collision complex with an energy greater than E_0.

The ratio of partition functions defined by Eqn (13) depends on temperature. There exists a boundary temperature T_k at which

the ratio is close to unity. At $T > T_k$, the processes in the collision complex become rate-limiting and the bimolecular rate constant is determined by the redistribution of energy.

Turning now to specific examples, we may note that calculations of T_k by Eqn (13) yield 800–1400 K for the $N_2O^* + CO$ and $N_2O^* + NO$ reactions depending on the hypotheses concerning the parameters of the activated complex.[73]

Thus the manifestation of nonequilibrium effects in bimolecular exchange reactions of polyatomic molecules depends greatly on the relation between the rate-limiting stages presented in Eqn (13) and is most probable for fairly high temperatures.

We may note, incidentally, that the deviations of the bimolecular rate constants from the equilibrium values are less pronounced than for the unimolecular decomposition reactions (Fig. 13). This is apparently one of the reasons why the nonequilibrium effects in bimolecular reactions were assumed to be relatively insignificant and did not receive sufficient attention.

One may postulate that the collision-stochastic model of bimolecular reactions is capable of yielding satisfactory results also for laser-stimulated reactions.

As an illustration, we shall consider the calculations for the reactions of BCl_3 molecules, excited by IR laser radiation, with H_2 molecules (energy $\sim$ 1 J per pulse, duration of pulse 0.2 μs),[130] which confirms the principal postulates of the collision-stochastic model for bimolecular reactions. At a sufficiently high level of excitation, the chlorine atoms in the BCl_3 molecule are considered to have lost their permanent locations (as happens in the melting process in a solid) and they then move more independently and within the limits of the molecule may have significantly longer 'free paths'. The 'partly free' chlorine atom subsequently reacts with the incoming H_2 molecule:

$$BCl_3 + H_2 \xrightarrow{k_1} BHCl_2 + HCl\,. \qquad (14)$$

Several assumptions, taking into account the limitations to the mobility of the reactants within the limits of the initial molecules, are used in the calculations.

This model is a natural development of the ideas concerning the influence of the stochastic nature of the vibrations on the occurrence of bimolecular reactions and furthermore, as regards calculation, it represents a successful example of the application of relations employed in gas-phase and liquid-phase kinetics. In conformity with the model adopted, the reaction rate constant k_1 may be written in the form

$$k_1 = P_1 \upsilon_1 Q_1 \exp\left(-\frac{E_1}{T_1}\right),$$

where P_1 is the probability of the reaction

$$Cl + H_2 + 0.04\ eV \xrightarrow{k_2} HCl + H\,,$$

υ_1 is the average relative velocity of BCl_3 and H_2, Q_1 is the overall cross-section for the collision of H_2 and BCl_3, E_1 is the activation energy for the reaction, and T_1 is the thermal energy of the H_2-BCl_3 'reacting mixture'. The reaction probability P_1 can be written in the form

$$P_1 = Z_{12} k_2 n_2 t\,,$$

where Z_{12} is the steric factor for the reaction of chlorine and hydrogen within the limits of the collision complex and k_2 is the gas-phase rate constant:

$$k_2 = \upsilon_2 Q_2 \exp\left(-\frac{2650K}{T_2}\right),$$

where υ_2 is the relative velocity of BCl_3 and H_2, Q_2 is the overall scattering cross-section for the H_2-Cl system, T_2 is the temperature at the centre of mass of the incoming hydrogen molecule and chlorine in BCl_3, and n_2 is the density of chlorine atoms in BCl_3. The 'contact time' of the reactants is represented by the equation

$$t = \frac{1}{n_2 Q_2 \upsilon_2}\,.$$

The temperature of the chlorine atoms in this model is proportional to the kinetic energy of the atoms, equal to half the absorbed energy of the laser pulse (the second half represents the potential energy):

$$T_{Cl} = \frac{\hbar c n_\nu \bar{\nu}}{2 n_a (3/2) k_B} + T\,,$$

where n_ν is the number of quanta of the laser radiation absorbed by the molecule, $\bar{\nu}$ the energy of the radiation quantum in cm^{-1}, n_a the number of atoms in the 'hot molecule', k_B the Boltzmann constant, and $(3/2)k_B$ the heat capacity of the translational degrees of freedom.

In the example of the heating of BCl_3 by the radiation from a CO_2 laser (ν = 950 cm^{-1}, $n_\nu = 10$, $n_a = 4$) considered by Kueba and Wolfrum,[128] $T_{Cl} \simeq 1140\ K + T_1$ was obtained. The temperature at the centre of mass of the interacting H_2-Cl system is defined by the equation

$$T_{H_2-Cl} \approx T_{H_2}\left(1 + \frac{T_{Cl}}{T_{H_2}}\,\frac{M_{H_2}}{M_{Cl}}\right),$$

where T_{Cl} and M_{Cl} are respectively the temperature and the atomic weight of chlorine, $T_{H_2} = 300$ K, and M_{H_2} is the molecular mass of hydrogen. T_{H_2-Cl} is found to be relatively low ($\sim$ 380 K) for the parameters quoted above.

Calculations performed with the aid of the above relations for the collision-stochastic model agree well with experimental data for the laser stimulation of the BCl_3-H_2 reaction.

In conclusion we shall note the most significant characteristic features of the activation mechanism of bimolecular reactions.

1. The vibrational energy of a polyatomic molecule is particularly effective in the bimolecular interaction of the partners when the reaction barrier is higher than the threshold of the transition to stochastic motion.

2. The stochastic nature of the vibrational motion explains the phenomenon of the so called multiplicity of collisions in the interaction of partners (the concept of a differentiated reaction coordinate then loses its significance; all these features together with the effect of the mixing of the modes are responsible for the high pre-exponential factors for the equilibrium rate constants [see Teitelbaum [73] and Table 5)].

3. The existence of the 'translational barrier' for bimolecular HES reactions is in essence equivalent to the introduction of the temperature at the centre of mass of the 'hot' molecule and the 'cold' partner.[71]

The above comparison indicates the conditions under which the traditional versions of the transition state method fail to work and should be replaced by the collision-stochastic model.

XI. Conclusion

The 'hot' band absorption spectroscopy of molecules makes it possible to investigate the influence of the form of the energy distribution function and of the dynamic parameters of the molecules on their absorption spectra, which constitutes the basis for the observation of highly excited molecules. The data on the properties of the distribution function then obtained are used in the analysis of kinetic processes with participation of HES on the basis of the solution of the fundamental microkinetic equation.

The emission technique in the visible, UV and IR regions of the spectrum, both in the traditional version and especially with Fourier transformation by virtue of the high sensitivity and high

time resolution, is very promising for the probing of HES distributions in reacting systems with thermal and laser pumping. The linkage between the optically active emitting electronic states and the highly excited states of the ground electronic term provides an instrument for the detection of these states and the energy distributions within the limits of both terms by virtue of reverse electronic relaxation.

The possibility of calibrating the 'hot' band absorption and emission spectra of polyatomic molecules constitutes one of the most important preconditions for the successful application of these methods in the study of nonequilibrium HES distributions.

Measurement of the kinetics of the transformation of HES distributions on thermal or laser pulse excitation is most productive in the determination of the HES energy exchange parameters in collisions.

The most realistic description of experimental data on the HES energy exchange kinetics in collisions is based on the superposition of strong and weak collisions.

In order to create an integral picture of the energy exchange and reactions of HES and also for the development of generalising concepts, it is necessary to carry out a joint analysis of the information obtained on the basis of both direct spectroscopic methods and indirect kinetic methods.

In conclusion, we shall make several predictive comments. Firstly, the ratio of computational and experimental studies will steadily change in favour of the former; the contribution of trajectory calculations will increase greatly. Secondly, the most promising way of developing the theory of processes with participation of HES involves the combination of trajectory calculations and simple basic models. Thirdly, DF calculations will be closely related to the spectra of the reacting components and calculations of this kind will become a standard procedure for investigators in the field of molecular and chemical kinetics.

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