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Dynamics of Elementary Processes in Liquids

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The dynamics and mechanism of the basis elementary processes in a liquid have been examined, and their characteristic times (in the range 10^{-13}-10^{-6} s) compared. The relationship between these processes and their influence on the kinetics of chemical reactions has been discussed. The bibliography contains 120 references.

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I. DYNAMICS OF VIBRATIONAL RELAXATION

Information on the dynamics of the relaxation of vibrational energy in a liquid is obtained by analysing the line widths in the Raman and infrared absorption spectra or from molecular-acoustic ultrasonic absorption data. In the first case, a significant contribution to the line width is made by the rotational motion of the molecules; the procedure for taking account of this contribution and distinguishing the natural line width (which is determined by the lifetime of the vibrational quantum) is difficult and unreliable. Molecular-acoustic methods are also unreliable, since the absorption of high-frequency sound by the excitation of vibrational degrees of freedom is accompanied by the excitation of conformational transitions in molecules. For this reason, only data obtained for conformationally rigid molecules can be accepted with any confidence. The methods of acoustic and vibrational spectroscopy have established only that the vibrational relaxation times in a liquid lie in the picosecond range [1,2].

Direct measurements of the vibrational relaxation times in a liquid became possible with the appearance of lasers generating powerful single pulses of picosecond duration [3-11]. The principle of the measurement is as follows. A picosecond pulse of frequency ν_L, passing through the liquid being studied, undergoes Raman scattering, exciting intramolecular vibrations with frequency ν_M; the intensity of the scattered Stokes component of the radiation with frequency $\nu_L - \nu_M$ increases as the pulse passes through the substance. The concentration of

vibrationally excited molecules increases simultaneously for each photon of Stokes frequency $\nu_L - \nu_M$ there is one molecule in the first vibrationally excited state $v = 1$. The population of the state $v = 1$ after the passage of the exciting pulse reaches a value of $\sim 10^{-3}$, which is greater by 3–4 orders of magnitude than the thermodynamically equilibrium population. Subsequently, as a result of vibrational relaxation processes $v = 1 \rightarrow v = 0$, the above equilibrium population of the state $v = 1$ disappears with a characteristic time τ_1.

The kinetics of the change in the population of the state $v = 1$ are observed by means of a series of delayed probing picosecond pulses of low intensity and frequency νl. The intensity of the Antistokes component of the radiation with frequency $\nu l + \nu_M$, which is proportional to the population of the vibrationally excited level $v = 1$, is measured. The experimentally measured time corresponding to the decay of the Antistokes radiation is the vibrational relaxation time of the excited molecule.

Experiments of this type are usually carried out using the single picosecond pulse of a neodymium laser, which is divided into two parts. The more powerful part of the pulse passes through a KDP crystal to double the frequency and is used to excite molecular vibrations and Raman scattering in the liquid being studied. The second, weaker part of the pulse passes along a delay line consisting of an echelon—a series of plates of different thickness. The echelon forms a series of probing pulses delayed in time to detect the Antistokes radiation in the molecular vibrations generated by the main (exciting or pumping) pulse. In this version of the experiment, $\nu_L = 2\nu l$. It is also possible to double the frequency of the probing pulses, leaving the frequency of the pumping pulse unchanged, equal to the frequency of the neodymium laser; in this case, $\nu l = 2\nu_L$.

The picosecond pumping pulse ν_L and the Stokes radiation $\nu_L - \nu_M$ generated by it are coherent, so that the vibrational excitation of the molecules is also coherent. In other words, definite phase relationships exist between the vibrations of the excited molecules: they all vibrate in step, in the same phase. The phase synchronism of the vibrations gradually breaks down with a characteristic time τ_2; this leads to the loss of the coherence of the vibrations and the Antistokes radiation and is detected as a change in the coherence of the probing picosecond pulses.

There are thus two relaxation processes: the first characterises the loss of vibrational energy and takes place in a time τ_1; the second characterises the loss of the phase synchronism (coherence) of the vibrations and takes place in a time τ_2. Both are detected by the probing pulses from the intensity of the Antistokes radiation; the non-coherent part of this radiation is used for the former, and the coherent part for the latter. The non-coherent radiation is scattered isotropically and is usually measured at an angle of 90° to the direction of the pumping pulse; the coherent radiation is propagated and detected along the direction of the pumping pulse.

The experimental data on the dynamics of the vibrational relaxation of molecules in the ground electronic state can now be examined. For the N_2 molecule at −196°C with a fundamental vibrational frequency of 2336 cm^{-1}, $\tau_2 = 75 \pm 8$ picosecond (ps),[4] which agrees with the value 79 ± 8 ps found by analysing the width of the Raman line[12]. For the C–Cl symmetric stretch with frequency 459 cm^{-1} in CCl_4, $\tau_2 = 4 \pm 0.5$ ps,[13] which also coincides with the value 4 ps obtained from the Raman spectra. Thus the vibrational relaxation times measured from the Raman spectra are in fact the phase relaxation times.

The dynamics of the vibrational relaxation of the totally symmetric stretches of the CH_3 groups in CH_3-CCl_3 (frequency 2939 cm^{-1}) and in CH_3CH_2OH (frequency 2928 cm^{-1}) have been studied[14] at 300 K. With increase in the delay time of the probing pulses, the intensity of the Antistokes scattering increases at first, reaches a maximum, and then decreases exponentially (Fig. 1). The increase in intensity is due to pumping, and the decrease is due to vibrational relaxation. The coherent radiation decays much more rapidly than the non-coherent radiation: $\tau_1 = 5.2$ ps, $\tau_2 = 1.3$ ps (for CH_3CCl_3); $\tau_1 = 22$ ps, $\tau_2 = 0.26$ ps (for CH_3CH_2OH). Thus the ratios τ_1/τ_2 are 4 and 80 in CH_3CCl_3 and CH_3CH_2OH respectively. For N_2 in liquid nitrogen, $\tau_1 \simeq 1$ s, and the ratio τ_1/τ_2 is even greater ($\sim 10^{10}$).[15] This value is anomalously high; for most vibrations of polyatomic molecules studied in a liquid at room temperature, τ_1/τ_2 has values in the range 10–100.[5]

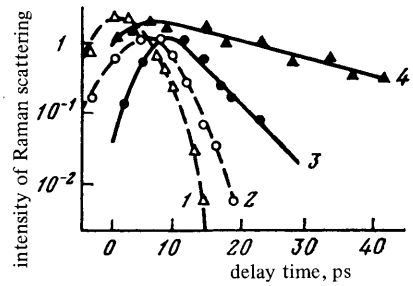


Figure 1. Kinetics of the phase (*1*, *2*) and energy (*3*, *4*) relaxation of the CH_3 stretching vibrations in CH_3CCl_3 (*2*, *3*) and in CH_3CH_2OH (*1*, *4*).[14]

This marked difference in the rates of the phase and energy relaxation is due to the difference in their physical mechanisms. Phase relaxation (loss of coherence of the excited vibrations) takes place as a result of the resonance transfer of a vibrational quantum from an excited to a non-excited molecule. Since the phases of the vibrations of the non-excited molecules are arbitrary and random, this transfer of vibrational energy is accompanied by phase correlation losses, that is loss of coherence. The vibrational quantum does not disappear, but is merely transferred from one molecule to another; its disappearance, that is its transfer to external degrees of freedom of the molecule, is a much slower process. Thus the times τ_2 and τ_1 characterise respectively the kinetics of the processes of the resonance transfer of vibrational energy and its relaxation into the lattice.

The results of experiments which show how the energy relaxation takes place can now be discussed. The energy of the stretching vibrations of the C–H bond correspond to a frequency $\nu_H \simeq 3000$ cm^{-1}, and the energy of the bending vibrations corresponds to a frequency $\delta_H \simeq 1500$ cm^{-1}, that is to half the energy of the stretching vibrations.

The simultaneous measurement of the kinetics of the population of the vibrationally excited states with frequencies 3000 cm^{-1} and 1500 cm^{-1} for the CH_3CCl_3 molecule have shown that excitation of the 3000 cm^{-1} vibration is accompanied by excitation of the 1500 cm^{-1} vibrations.

This means that the population of the excited levels of the bending vibrations takes place through the excited levels of the stretching vibrations. In other words, the relaxation of the 3000 cm^{-1} vibrational quantum takes place by its "exchange" for 1500 cm^{-1} vibrational quanta; the efficiency of this exchange is close to unity[16].

An even more illustrative example is provided by the CH_3CH_2OH molecule[17], which has 21 normal vibrations, five of them in the range 2972–2877 cm^{-1}. The picosecond pumping pulse excited the stretching vibration at 2928 cm^{-1}, and the probing pulses detected the Antistokes scattering on levels in the band 2830–3000 cm^{-1}. It was found that the excitation spectrum was fairly broad (~150 cm^{-1}) and covered almost the entire band of the levels 2830–3000 cm^{-1}. Excitation of the 1550 cm^{-1} and 1350 cm^{-1} levels, which correspond to bending vibrations in the first and second vibrational levels respectively, was also detected.

These results show that the excitation of one stretching vibration (at 2928 cm^{-1}) is very rapidly (in 0.5–1 ps) redistributed between closely situated vibrational levels (in the band 2830–3000 cm^{-1}). It is then transferred slowly (in 22 ps) to vibrational levels of the bending vibrations; from these levels the energy undergoes relaxation into the lattice even more slowly (in ~40 ps).[17]

Data[18] on the excitation of the stretching vibrations of the C–H bonds in hydrocarbons in a band of width 140 cm^{-1} close to 2900 cm^{-1} agree with these conclusions; the relaxation of the population of the excited vibrations was measured. The results are given in Table 1. If τ is normalised to the relative number of methyl groups in the molecule, the values of τ_{norm} obtained remain surprisingly constant in the hydrocarbon series (in particular, in n-heptane there are two methyl groups and seven carbon atoms, so that τ_{norm} = (11.0 ps. 2/7) = 31.14 ps).

Table 1. Vibrational relaxation times in hydrocarbons[18].

Compound	°C	τ, ps	τ_{norm}, ps
n-Heptane	20	11.0	3.14
	−25	14.0	
	−70	16.0	
n-Decane	20	16.0	3.20
	−25	21.0	
Isodecane	20	10.8	3.24
n-Tridecane	20	21.0	3.23
n-Pentadecane	20	24.5	3.27
Hept-1-ene	20	21 0	3.00
Dec-1-ene	20	33.5	3.35
Hepta-1,6-diene	20	60.0	—

This regular feature can be regarded as a consequence of the fact that the vibrational energy rapidly undergoes intramolecular redistribution and is lost through the methyl groups (preferentially through two quanta of the 1450 cm^{-1} bending vibrations).

Data on the transfer of vibrational energy between different molecules can now be examined. Laubereau and coworkers[16] studied relaxation in CH_3CCl_3 + CD_3OD mixtures. On excitation of the stretching vibrations ν(C–H) 3000 cm^{-1} in CH_3CCl_3, it was found that the vibrations ν(C–D) ≃ 2200 cm^{-1} of the CD_3OD molecule are excited, that is intermolecular transfer of a vibrational quantum takes place. Its efficiency depends on the composition of the mixture; the transfer of energy requires the interaction of three particles: an excited CH_3CCl_3 molecule, a non-excited CH_3CCl_3 molecule, and a non-excited CD_3OD molecule. It is assumed that this complex interaction is required in order to establish quasi-resonance conditions for the transfer of energy, since ν(C–H) ≃ ν(C–D) + ν(C–Cl). To satisfy this condition, however, the bimolecular interaction CH_3CCl_3 + CD_3OD is sufficient, since the excess vibrational quantum, equal to ν(C–H) − ν(C–D) may undergo intramolecular transfer to a C–Cl bond of the original CH_3CCl_3 molecule excited in the C–H vibration. A role in the transfer of the vibrational quantum may be played by the bimolecular interaction of the excited CH_3CCl_3 molecule with a van der Waals molecule (CH_3CCl_3 + CD_3OD) (for van der Waals molecules see part V).

In a mixture of CH_3CCl_3 and CD_3OD (60:40), the transfer of energy to CD_3OD takes place with τ_1 ≃ 13 ps and with a probability of 0.5; the other half of the vibrational energy of CH_3CCl_3 undergoes intramolecular relaxation through the bending vibrations of the CH_3 group.

In CH_3CCl_3 + CCl_4 mixtures with mole fractions of CH_3CCl_3 (x) equal to 1, 0.8, 0.6, and 0.4, the relaxation time of the vibration ν(C–H) ≃ 3000 cm^{-1} in CH_3CCl_3 increases from 5.2 ps to 29 ps according to the law $\tau^{-1} \sim x^2$ with decrease in x from 1 to 0.4;[16] that is in this case the relaxation of the vibrational energy is a termolecular process: one excited CH_3CCl_3 molecule interacts with two non-excited molecules; the CCl_4 molecules are inert and do not take part in the vibrational relaxation, since the vibrational quantum of the C–Cl bond (≲800 cm^{-1}) is small compared with the quantum being relaxed (~3000 cm^{-1}). In this case the relaxation of the energy possibly involves the van der Waals molecule (CH_3CCl_3 + CH_3CCl_3).

The lifetime of the vibrationally excited level of benzene with frequency 991 cm^{-1} (a totally symmetric vibration) is 5 ps, and increases to 8 ps when benzene is diluted with deuterobenzene[19].

The dynamics of vibrational relaxation in electronically excited states of molecules can now be examined. The fluorescence of Rhodamine 6G is delayed relative to an exciting laser pulse[20,21]. The delay is due to the fact that the exciting pulse populates high-lying vibrational levels of an excited singlet state of the molecule, and the fluorescence takes place from the ground vibrational level. These two events—excitation and fluorescence—are separated by a time interval τ, during which the vibrational relaxation of the excited singlet takes place, that is the molecule "descends" from the excited vibrational levels into the ground vibrational level of the electronically excited singlet state.

Quantitative measurements of τ have been carried out for several molecules[22]. A picosecond pulse of frequency ν_L excited the Rhodamine 6G molecule into high vibrational levels of the excited singlet, after which the probing picosecond pulses detected the intensity of the fluorescence from lower-lying vibrational levels at a frequency $\nu_l < \nu_L$ (ν_l usually coincided with the frequency of the centre of the fluorescence band). Thus an inverted population of the vibrational levels of the excited singlet is first created, after which vibrational relaxation restores the normal distribution of the populations; the kinetics of the restoration are detected from the increase in the intensity of the probing picosecond pulses with the passage of time. For Rhodamine 6G in ethanol, the restoration time (that is the vibrational relaxation time in the excited singlet) was 8.3 ps.[22] For the molecules of Erythrocin B, this time was much smaller (τ < 2 ps) and could not be measured[23]. For the molecule of azulene, excited into vibrational levels

lying ~5000 cm^{-1} above the ground level, relaxation to the ground vibrational level takes place with a characteristic time of 7.4 ps;[24] for the vibrational levels lying 500 cm^{-1} above the ground level, this time is 4 ps.[25]

Thus vibrational relaxation in electronically excited states of molecules takes place in a time comparable with or slightly shorter than the vibrational relaxation time of the molecules in the ground electronic state.

II. ROTATIONAL MOLECULAR MOTION

Both physicists and chemists have carried out extensive and successful studies of the rotational–orientational dynamics of molecules in a liquid. Only the most fundamental results will be examined here: 1) the relationship between molecular rotation and the macro-properties of a liquid (in particular, the macro-viscosity); 2) the way in which rotation and reorientation of the molecules take place, and models of this motion; 3) the problem of whether there is a correlation between the rotational and translational motion, and the nature of their relationship; 4) the reorientation of the vector of the angular momentum of rotation; 5) and 6) the quantitative scale of the rotational frequencies.

Before discussing these questions, the physical phenomena on which methods for studying rotational motion are based can be examined. The thermal motion of the molecules in a liquid produces fluctuations in the anisotropy of the polarisability, when the molecules in a small element of volume are randomly found in identical orientations. This fluctuation represents the optical non-uniformity on which scattering of light takes place. Since the fluctuations themselves are oriented randomly, the vectors of their polarisabilities are also directed randomly; this means that the scattered light will be depolarised. The creation and disappearance of fluctuations in the anisotropy take place as a result of the orientational–rotational movements of the molecules, so that the scattered light will be modulated by the frequency of these movements; information on the frequency of the modulation is obtained from an analysis of the line shape in the scattering of the depolarised light. This phenomenon is known as Rayleigh light scattering[26].

Another optical method for studying the rotation of molecules is based on the depolarisation of fluorescence. If isotropically distributed molecules are excited by linearly polarised light, only those molecules will be excited which are oriented in such a way that the dipole moment of their optical transition is directed along the vector of the electric field of the exciting light. Thus the electronically excited molecules have a non-uniform distribution of orientations. If the molecules were stationary, the emission of the fluorescence would have the same polarisation as the exciting light. Molecular rotation, however, leads to random distribution of the orientations of the excited molecules and to depolarisation of the fluorescence. The degree of depolarisation is directly related to the frequency of the molecular rotation.

Both stationary and pulse methods of magnetic radio-frequency spectroscopy (EPR and NMR) are widely used to study rotational dynamics in a liquid. Information on the dynamics is obtained from an analysis of the EPR or NMR line widths and from the electronic or nuclear relaxation times. Both the line widths and the magnetic relaxation times are determined by the intramolecular dipole or quadrupole interactions, the magnitude of which depends on the orientation of the molecule or radical in the magnetic field. Molecular rotation changes the orientations of the particles and modulates the extent of the magnetic interactions; in other words, the molecular rotation modulates the magnitude and direction of the local magnetic fields acting on the electron or nucleus. The line widths and relaxation times depend on the magnitude of the magnetic interactions and the frequency of their fluctuations; if the magnitude of the interaction is known (this is usually the case), the experimentally measured line widths or relaxation times are used to calculate the characteristic times of the rotational–orientational movements.

Mention may also be made of the classical methods of dielectric relaxation, which measure the reorientation times of the electric dipoles of the molecules, and also the methods of Raman light scattering and infrared (vibrational) spectroscopy. In the last two cases, information on the dynamics of rotation is obtained from an analysis of the width of the line and its wings. Finally, the new methods of picosecond spectroscopy may be mentioned.

The questions listed at the start of this section can now be discussed.

1. Relationship Between Molecular Rotation and the Macro-properties of a Liquid

The coefficient of rotational diffusion D_{rot} is determined by the classical relationship

$$D_{rot} = kT/\xi, \tag{1}$$

where ξ is the coefficient of friction experienced by the rotating molecule. In the Debye theory of dielectric relaxation, the coefficient of friction for spherical molecules was calculated from the equations of classical hydrodynamics[27,28]:

$$\xi = 8\pi\eta a^3, \tag{2}$$

where a is the radius of the rotating particle, and η the viscosity of the medium.

On the other hand, molecular rotation is a random stochastic process; it follows from the theory of these processes that the characteristic time of rotational reorientation τ_θ is related to D_{rot} by the following expression:

$$\tau_\theta = (6D_{rot})^{-1}. \tag{3}$$

Substitution of Eqns. (1) and (2) in Eqn. (2) gives the familiar Debye–Stokes–Einstein relationship

$$\tau_\theta = \frac{V\eta}{kT}, \tag{4}$$

which establishes the relationship between the rotational reorientation time of the molecules and the macroscopic viscosity of the medium. This approach was later extended by Perrin[29] to the rotation of ellipsoidal molecules.

A large number of studies have established reliably that the linear relationship between τ_θ and η/T, predicted by this expression, is always observed, but the volumes of the molecules V calculated in this way often do not agree with the actual dimensions of the molecules. In other words, Eqn. (4) gives unsatisfactory quantitative results. Thus depolarised Rayleigh light scattering for the molecules of benzene, toluene, and xylene in different isotropic non-solvating solvents showed[30] that τ_θ obeys the equation

$$\tau_\theta = C\eta + \tau_0, \tag{5}$$

where the constant C was smaller by a factor of 2–6 than that predicted by Eqn.(4); the value of τ_θ, as expected, is close to the period of rotation of the free classical rotator τ_R:

$$\tau_\theta \simeq \tau_R = \frac{2\pi}{9}(I/kT)^{1/2}. \quad (6)$$

In the great majority of cases, Eqn.(4) predicts values of τ_θ which are greater by an order of magnitude than the experimental values. Moreover, the activation energies of rotation (E_θ) are also frequently found to be smaller than the activation energies of the viscosity (E_η), although Eqn.(4) predicts that $E_\theta = E_\eta + RT$. Finally, Eqn.(4) predicts that the dependence on the hydrostatic pressure should be the same for τ_θ and η, whereas the experimentally measured relationships are different [31].

Eqns.(2) and (4) were derived from the equations of classical hydrodynamics for a sphere of volume V, rotating in a continuous medium; clearly, they do not take account of the molecular structure of the liquid, so that in principle it cannot be required that Eqn.(4) give the rotational dynamics quantitatively. In order to "adapt" Eqn.(4) for a correct description of the experimental results, the concept of micro-viscosity η^* was introduced. The quantity η^* is related to the macro-viscosity by the expression $\eta^* = f\eta$, where the coefficient f is a correction for the micro-viscosity. Gierer and Wirtuz [32], in the quasi-stationary approximation, calculated the rotational moments acting on a rotating molecule of radius a from neighbouring molecules of radius b, and determined the coefficient

$$f = \left[6\left(\frac{b}{a}\right) + \left(1 + \frac{b}{a}\right)^{-3}\right]^{-1}. \quad (7)$$

In the simplest case, $b = a$, so that $f = 0.16$; in general, $f \leq 0.16$ (for example, for benzene, dioxan, and cyclohexane, $f \simeq 0.06-0.08$). [32] The correction for the micro-viscosity is introduced semi-empirically, and must be determined experimentally for each rotating molecule–solvent pair.

Considerable progress was made by Steele [33], who developed a theory for calculating the coefficient of friction not from hydrodynamics but at a molecular-kinetic level. It is assumed that the particle moves under the influence of a randomly fluctuating rotational moment; the fluctuations are due to the angular dependence of the intermolecular potential. Since the intermolecular potential of a particle in the environment created by its neighbours is in general anisotropic, the coefficient of friction ξ in Eqn.(1) becomes a tensor quantity; the calculation of the components of the tensor in terms of the parameters of the intermolecular potential is a complex unsolved problem. For the particular case of molecules of the spherical top type, Steele [33] obtained the expression

$$\xi_{ii}^2 = \frac{2I}{\pi}\left\langle \frac{\partial^2 W(R, \Psi)}{\partial \psi_i^2} \right\rangle, \quad (8)$$

where ξ_{ii} is a component of the tensor ξ, I the moment of inertia, and $W(R, \Psi)$ the potential, which is a function of the distance and the angle; the averaging is carried out over all the other variables; in the laboratory system of coordinates, $i = x, y, z$. Eqn.(8) shows that the principal components of the tensor ξ (ξ_{xx}, ξ_{yy}, ξ_{zz}) are proportional to the second derivative of the intermolecular potential with respect to the angle of rotation about the chosen axis.

In recent years there has been a new approach to the calculation of τ_θ within the framework of hydrodynamics [34]. In the derivation of Eqn.(4) it was assumed that the sphere rotates in the continuous medium together with the boundary layer; in other words, it was assumed that the sphere is rigidly bonded to the boundary layer. In fact, this condition is not necessary: the particle may slip relative to the boundary layer. This is equivalent to a decrease in the coefficient of friction and a decrease in τ_θ. The same approach was also deveoped for calculating the coefficient of friction for the rotation of ellipsoids [34] and molecules of arbitrary shape [36]. In particular, for a symmetrical ellipsoid

$$\xi_{xx}^* = \frac{32\pi\eta a^3}{25} e^2 \left(1 - \frac{74}{25} e\right), \quad (9)$$

where a is the length of the semi-axes x and y, and c the length of the semi-axis z; $e = (a/c)^2 - 1$. Fig.2 shows that the ratio ξ_{xx}^*/ξ_{xx} depends on the form of the ellipsoid; here ξ_{xx}^* is determined by Eqn.(9) in the model involving slip, and ξ_{xx} is calculated from the Perrin equations in the hydrodynamic model (without slip). It can be seen that the differences in the coefficients of friction in these two models depend to a marked extent on the shape of the molecules. For an ideal spherical molecule ($a/c = 1$), the model involving slip gives $\xi_{xx} = 0$, that is it predicts free rotation.

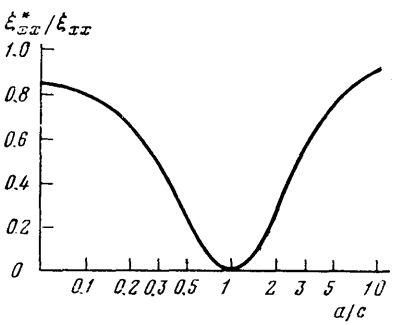


Figure 2. Plot of ξ_{xx}^*/ξ_{xx} against a/c. [37]

This result agrees with Steele's theory: if the intermolecular potential is spherically symmetrical, it follows that $(\partial W/\partial\psi) = 0$, so that from Eqn.(8) it follows that $\xi_{xx} = 0$. In actual fact, molecules with an ideally symmetrical spherical potential do not exist, although many real molecules (CH_4, CCl_4, etc.) have a potential which is almost symmetrical, so that their rotation is restricted to only a slight extent. The hydrogen molecules also undergoes free rotation about the axis directed along the H–H bond, since $\xi_{HH} \simeq 0$. Bauer and coworkers [38] compared the experimental $\tau_\theta(\eta)$ relationships obtained for different molecules by Rayleigh light scattering and NMR relaxation with the theoretical values. It was found that the model including slip reproduces the experimental $\tau_\theta(\eta)$ relationships with good accuracy (±20%).

An interesting feature is that the best agreement is obtained in systems in which there are no solvation effects. In systems where there is strong solvation (for example strong hydrogen bonds), the experimental results are best reproduced by Eqn.(4), that is by the model with rigid binding. Physically, this tendency is wholly reasonable: clearly, solvation will not influence molecular rotation if the lifetime of the complex (or coordination solvate sphere)

is much smaller than τ_θ. On the contrary, stable complexes will rotate as a whole. The dimers of carboxylic acids rotate as a whole in CCl_4;[39] on the other hand, t-butyl alcohol does not influence τ_θ for nitrobenzene[40], since complex formation in this system is weak.

EPR and NMR have been used[41] to study the rotational dynamics of the complex of the stable nitroxide radical with chloroform in various alcohols. A correction for the micro-viscosity was introduced experimentally, and it was shown that the comparatively stable radical–chloroform complex pairs rotate in alcohol as a whole, and the calculated volumes of the rotating particles correspond to their geometric dimensions.

The hydrodynamic model of rotation with slip describes satisfactorily not only the viscosity relationships $\tau_\theta(\eta)$ but also the temperature dependence $\tau_\theta(T)$. As a rule, in systems with slip, $\epsilon_{rot} < \epsilon_\eta$, whereas in systems without slip, $\epsilon_{rot} \simeq \epsilon_\eta$.

2. Models of the Rotation of Molecules in a Liquid

The orientational–rotational movement of a molecule is accompanied by a change in the angular orientation of its axes. It may be assumed that in a time τ_θ the change in the angle is θ; this change may take place either by continuous slow rotation or by a single instantaneous abrupt rotation through an angle θ. Thus in principle it is possible to picture two models of molecular rotation: Brownian diffusion, when the reorientation of the axis of the molecule takes place continuously and randomly, and discontinuous abrupt large-amplitude diffusion. Brownian rotational diffusion can also be regarded as a continuous sequence of abrupt movements of infinitely small amplitude; the difference between the two models of the motion then reduces to a difference in the amplitudes of the elementary abrupt rotational movements.

It is not difficult to understand the physical mechanism of Brownian diffusion (even within the framework of hydrodynamic ideas); it is more difficult to determine the causes and mechanism of abrupt movements of large amplitude. One mechanism[42] assumes that a molecule in a liquid rotates only at those moments when a random fluctuation gives a sufficiently large free volume around it; at these moments the movement of the molecule is regarded as the rotation of a free rotator. When the fluctuation in the free volume disappears, the environment around the molecule contracts, and it remains until the next fluctuation. Theoretical analysis of this mechanism leads to a number of conclusions. Firstly, the activation energy of the rotation must be close to the work of forming the fluctuation of the free volume; this is usually a small quantity, smaller than the activation energy of the viscosity. Secondly, since the rotating molecule is regarded as a free rotator, τ_θ in this model should depend on the moment of inertia of the molecule, so that for isotopically substituted molecules, an isotopic effect in τ_θ should be observed. Atkins and coworkers[42] found that the ratio of τ_θ for the ND_3 and NH_3 molecules is 20% greater than that expected from Eqn.(4); the ratio $\tau_\theta(ND_3)/\tau_\theta(NH_3)$ was found to be close to the ratio $[I_\perp(ND_3)/I_\perp(NH_3)]^{1/2}$, where $I_\perp$ is the component of the moment of inertia perpendicular to the axis of symmetry of the molecule. This is the isotope effect predicted by the theory.

Another mechanism[43,44] assumes that the immediate environment of the molecule has the structure of the crystal lattice, so that the molecule may undergo a reorientation of large amplitude only with the condition that a structural defect or vacancy is created around it, as a result of the displacement of one of the neighbouring molecules into an adjacent lattice site. In this theory, the activation energy of rotation includes the work of formation of the vacancy, and the volume of activation includes the volume of activation for translational diffusion. The first quantity should be close to the molar heat of volatilisation, and the second should be close to the molar volume of the vacancy. The experimentally determined values of these quantities are respectively only 17% of the molar heat of volatilisation and 26% of the molar volume of the vacancy.

Thus the model of the fluctuating free volume shows better agreement with experiment; as will be seen later, this model is also confirmed by the pressure dependence of τ_θ.

How is it possible to establish whether the particle is rotating by a Brownian diffusion mechanism or in abrupt movements? Before answering this question, it is necessary to consider the determination of the coefficient of rotational diffusion D_{rot}.

Eqn.(3) represents a particular definition of D_{rot}; in the general case,

$$D_{rot} = 1/l(l+1)\tau_\theta. \qquad (10)$$

The quantity D_{rot} is a universal characteristic, and is determined by the properties of the rotating particle–medium system; D_{rot} is independent of the physical method of measuring τ_θ. Different methods measure different values of τ_θ, however, and therefore correspond to different values of l (see later).

This important question must be dealt with briefly. All physical methods (mentioned at the start of this section) measure the time dependence of some interaction; usually, the interaction is a random function of time, and its time dependence is described by introducing a correlation function, which characterises the rate at which the "memory" of the magnitude of the initial interaction is lost. It is usually assumed that the correlation function decreases exponentially with a characteristic time τ_θ. In other words, τ_θ is the time in which the magnitude of the interaction changes by a factor of e as a result of molecular rotation. It may be assumed that in this time the "memory" of the magnitude of the initial interaction is lost, that is the correlation disappears; for this reason, τ_θ is called the correlation time of the rotational motion.

The correlation function is expressed in terms of special functions—spherical harmonics of rank l. For interactions of the vector type, $l = 1$; these include the interaction of a constant dipole electric moment with an electric field. For interactions of the tensor type, $l = 2$; these include the dipolar interaction of the nuclei (in NMR), electron–nuclear dipolar interaction (in EPR), and polarisability (in Rayleigh light scattering). Eqn.(3) is obtained from Eqn.(10) for $l = 2$; for dielectric relaxation, $l = 1$ and $\tau_\theta = (2D_{rot})^{-1}$.

From the definition (10) it now follows immediately that for Brownian diffusion

$$\tau_\theta(l=1)/\tau_\theta(l=2) = 3\ . \qquad (11)$$

In other words, if τ_θ is measured in a given system by two different methods, the ratio of τ_θ obtained should be equal to 3. One of the methods should measure an interaction of the vector type (for example from the dielectric relaxation or from an analysis of line shape in the infrared vibrational spectrum), and the other method should use an interaction of the tensor type (for example EPR, NMR, or Rayleigh or Raman light scattering).

The physical significance of Eqn.(11) is that in the rotation of the molecule, the tensor interaction changes more rapidly, so that the change in this interaction takes place e times more rapidly, in a shorter time τ_θ.

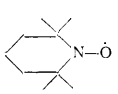
If the molecule rotates in abrupt movements with an amplitude which is sufficiently large for any interaction to change by a factor of not less than e, it follows that in this case τ_θ will be independent of the physical method of measurement; in this case

$$\tau_\theta(l = 1)/\tau_\theta(l = 2) = 1 . \qquad (12)$$

Eqn.(11) is applicable for Brownian diffusion, and Eqn.(12) for diffusion by abrupt movements; by determining the ratio $\tau_\theta(l = 1)/\tau_\theta(l = 2)$ experimentally, it is possible to reach conclusions regarding the mechanism of rotational diffusion. This approach, and a rigorous theory, were developed by Valiev and Ivanov [45].

The mechanism by which rotation of the molecule takes place can now be examined. Gershon and coworkers [46] determined τ_θ by Rayleigh light scattering in a number of liquids, and compared the results with the dielectric relaxation times. It was found that in quinoline, nitrobenzene, chlorobenzene, aniline, and pyridine at 25°C, the ratio of these times is close to unity. It was therefore concluded that the rotation of the above molecules takes place in abrupt movements with a large amplitude (~1–1.5 radian). On the other hand, the rotation of the molecules of nitrobenzene and camphor in CCl_4 and CS_2 takes place by a diffusion mechanism: for these molecules, the ratio $\tau(l = 1)/\tau(l = 2)$ is 3 ± 0.5. [45]

Recently, particular attention has been paid to the study of the rotation of nitroxide radicals, which are widely used as spin markers and probes [47,48]: the form of their EPR spectrum is sensitive to the model of rotation. It was found that the radical $(SO_3)_2^{2-}NO$ in aqueous glycerol rotates in almost abrupt movements [49], whereas the rotation of the molecule of spin-labelled haemoglobin is more effectively described by a continuous diffusion model [50]. In a study of a number of radicals of different shape and size, Kuznetsov [51] showed that the rotation of small radicals is described more effectively by the model of diffusion by abrupt movements, whereas that of large and unsymmetrical radicals is described more effectively by the continuous diffusion model [51]. For the radical



the conclusion that it undergoes abrupt movements was confirmed by comparing the values of τ_θ obtained from dielectric relaxation and from the EPR spectra [52]; their ratio being close to unity. A general tendency is for large and asymmetric molecules in viscous solutions to rotate by continuous diffusion; small molecules in non-viscous solutions generally rotate by abrupt movements.

In general, in a liquid, rotational movements of different frequency, scale, and amplitude are allowed, but movements of particular frequencies and amplitudes predominate, depending on the viscosity, temperature, size, and shape of the molecules. The movement of large molecules at high viscosities takes place with a low amplitude, and rotation through a large angle is made up of a large number of rotations through small angles; this is the case of continuous diffusion. With decrease in the viscosity, movements with large amplitude begin to predominate, and in the limit these can be regarded as abrupt movements. Situations intermediate between these two limiting cases are possible.

3. Relationship Between Rotational and Translational Motion

Data on the relationship between rotational and translational molecular motion in a liquid can be obtained by NMR relaxation. Studies of this kind have been carried out by Jones and coworkers [31], who studied the pressure dependence of the intramolecular dipole contribution to the relaxation of the protons of the molecules of acetone, benzene, chlorobenzene, toluene, and other derivatives of benzene, dissolved in the corresponding deuterated compounds. The intramolecular dipole contribution to the nuclear relaxation is determined only by the rotation of the molecules, and its pressure dependence shows unambiguously that the rotation depends on pressure.

The proton relaxation times of acetone and benzene are independent of pressure up to pressures of several kilobars. This means that the freezing of the translational mobility of the molecules at high pressures does not influence their rotational mobility, that is the rotation of these molecules is autonomous and independent of their translation. The physical cause lies in the fact that in these molecules the main contribution to the nuclear relaxation is made by rotations of the methyl groups (in acetone) and rotation of the benzene molecules about the C_6 symmetry axis; these movements also take place in the solid.

In substituted benzenes, where the symmetry of rotation is destroyed, the intramolecular dipole contribution to the nuclear relaxation shows a marked pressure dependence. In these molecules, rotation is related to translational motion; the relationship is stronger, the greater the van der Waals radius of the substituent in the aromatic ring.

Thus in the relationship between rotation and translation, the principal role is played by the shape of the molecules: for symmetrical molecules, rotation is practically autonomous, whereas for asymmetric molecules there is a marked correlation between these two types of molecular motion. This conclusion is confirmed by data on the scattering of slow neutrons by the liquid; in this case the theory which does not take account of statistical correlation of rotational and translational motion provides a poor description of the experimental data [53].

The correlation of the rotational and translational motion is quite natural; for a given molecule to rotate, it is necessary to have a fluctuation of the free volume around it, and this fluctuation is impossible without rotational–translational movement of its neighbours.

4. Behaviour of the Rotational Moments of Molecules

Exceptionally important information on the dynamics of molecular motion is given by NMR in those cases where the nuclear relaxation takes place as a consequence of spin–rotational coupling. A randomly rotating molecule is a system of moving charges, and therefore creates its own randomly varying electromagnetic field, the magnetic component of which induces the relaxation of the nuclei of the molecule. The correlation time of this spin–rotational coupling is the time corresponding to the change in the angular momentum of the molecule τ_J; in fact, this is the time which is necessary for the molecule to lose the "memory" of its original angular momentum or, in other words, it is the time between the collisions of the molecules in the liquid. The determination of the relationship

between the times τ_θ and τ_J is of particular importance for an understanding of the mechanism of molecular motion.

The behaviour of the angular momentum can be described by two different models[54]. One of these (the J-model) assumes that τ_J is the average time between instantaneous molecular collisions in which there are simultaneous changes in the magnitude and direction of the angular momentum. The other (the M-model) assumes that only the direction of the momentum changes, and that its magnitude (and hence the rotational energy) does not change. The results of the theoretical calculation of τ_J and τ_θ for these models are given in Fig. 3.[55]

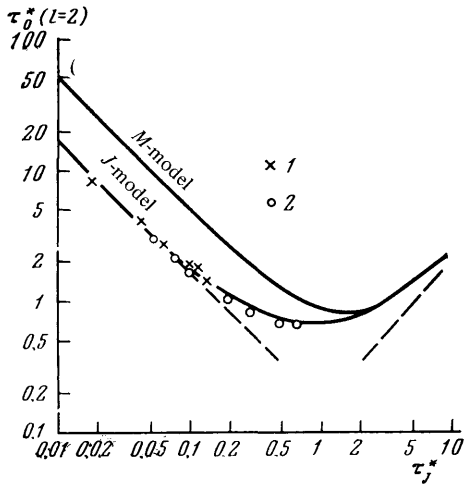


Figure 3. Relationship between τ_θ^* ($l = 2$) and τ_J^* in the J- and M-models[55]. The points give the experimental data: *1*) CS_2 (167–308 K), *2*) ClO_3F (140–368 K); $\tau^* = \tau(kT/I)^{1/2}$.

In the range of Brownian continuous diffusion $\tau_J \ll \tau_\theta$, and they are related by the expressions

$$\tau_J\tau_\theta = I/l\,(l+1)\,kT \qquad (13)$$

for the J-model and

$$\tau_J\tau_\theta = 3I/l\,(l+1)\,kT \qquad (14)$$

for the M-model (I is the moment of inertia of the molecule). These relationships are also obtained from the Langevin equations for the classical mechanics of a rotator[37]; Eqns. (13) and (14) also lead to the characteristic of Brownian diffusion already discussed [Eqn. (11)].

In the range of diffusion by abrupt movements, Eqns. (13) and (14) no longer apply (as expected), and τ_J is comparable with τ_θ; the physical significance of this result corresponds to the definition of diffusion by abrupt movements. This region lies close to the critical conditions for the existence of the liquid, and in this region the two models (J and M) give similar results. In the gaseous phase, according to kinetic theory, $\tau_\theta \sim \tau_J$ (Fig. 3).

The points in Fig. 3 give the experimental results for the ClO_3F and CS_2 molecules[56,57]. For ClO_3F, the value of τ_θ was determined from the relaxation of ^{35}Cl nuclei, induced by quadrupole coupling ($l = 2$), and τ_J was obtained from the relaxation of ^{19}F nuclei, taking place as a result of spin–rotational coupling[56]. At low temperatures, $\tau_\theta \gg \tau_J$, and Eqn. (13) is fulfilled, that is the rotation of the molecule takes place by the Brownian mechanism; at high temperatures, τ_θ is comparable with τ_J, and rotation takes place by abrupt movements. In CS_2, the relaxation of the ^{13}C nuclei takes place as a result of spin–rotational coupling and the anisotropy of the chemical shift[57]; both contributions have been measured, and the values of τ_θ and τ_J given in Fig. 3 obtained.

Similar measurements of τ_θ and τ_J have been carried out for the molecules of fluorobenzene, fluorine, CF_4, CCl_3F, HCl, SF_6, HBr, PH_3, CH_4, etc.[55] In all cases the J-model is applicable, that is paired collisions of the molecules are accompanied by simultaneous changes in the magnitude and direction of the angular momentum; the actual collisions take place randomly, and are not correlated. The applicability of the J-model confirms the view that there is a high efficiency of exchange of energy between the rotational and translational degrees of freedom.

The temperature dependence of τ_J is of interest. Since increase in temperature leads to an increase in the thermal velocities, it was expected that the time between the collisions of the molecules in the liquid should decrease, that is τ_J should decrease. Experiment reveals the opposite tendency. Thus for liquid fluorine at 56 K (m.p. 53.5 K), $\tau_J = 9.5 \times 10^{-14}$ s and increases with increase in temperature with an activation energy of 300 cal mole^{-1}.[58]

For fluorobenzene, τ_J also increases with increase in temperature, even at a constant density, that is for a constant intermolecular distance (experiments at high pressures)[31]; a similar increase in τ_J has been observed for CF_4, ClO_3F, etc. To explain this phenomenon, it was necessary to assume that the radius of the particles decreases with increase in temperature. In other words, with increase in the kinetic energy of the molecules, the distance of their maximum approach on collision decreases, that is more extensive overlap of the electron clouds of the colliding particles takes place. This corresponds to an increase in the free path of the molecules and hence to an increase in τ_J.

Eqns. (10) and (13) can be used to obtain the equation

$$D_{rot} = \left(\frac{kT}{I}\right)\tau_J, \qquad (15)$$

in which (kT/I) is the square of the angular velocity of the rotation, and τ_J the time between the collisions which lead to a change in the rotational moment and angular velocity.

The results given in Fig. 3 and in Eqns. (13) and (14) are of particular practical importance. They make it possible to estimate the values of D_{rot} and τ_θ from τ_J; τ_J in turn can be estimated from the thermal velocity of the molecules v and from the intermolecular distance d: $\tau_J \simeq dv^{-1}$. Here, $d = \bar{r} - \sigma$, where $\bar{r}$ is the average distance between the centres of the molecules, and σ the diameter of the molecule, which can be found from data on the elastic scattering, from molecular models, or from the molar volume of the solid:

$$\bar{r} = \left(\frac{V\sqrt{2}\cdot V}{N}\right)^{1/3}; \quad v = \left(\frac{8kT}{\pi m}\right)^{1/2};$$

V is the molar volume of the liquid, and N Avogadro's number. For a molecule of the benzene type, $\sigma \simeq 5.2$ Å, $\bar{r} \simeq 6.0$ Å, $v \simeq 6 \times 10^4$ cm s^{-1}, and $\tau_J \simeq 1 \times 10^{-13}$ s.

5. Anisotropy of the Molecular Rotation

Spherical molecules rotate isotropically, whereas the rotation of non-spherical molecules must be characterised by a rotational diffusion tensor. From the definition (8) of the components of the tensor coefficient of friction it follows that there are two factors responsible for the anisotropy of the rotation: the anisotropy of the force potential $\partial W/\partial\psi$ and the anisotropy of the moment of inertia I, the components of which, I_{xx}, I_{yy}, and I_{zz}, may in general be different.

The axes of symmetry of a molecule usually coincide with the axes of symmetry of its force field and the axes of the tensor of the moment of inertia, so that the principal components of the tensor of the rotational diffusion are the frequencies of rotation about the axes of symmetry. If the molecule has no axes of symmetry, the principal axes of the tensor of the rotational diffusion usually coincide with the principal axes of the tensor of the moment of inertia (with the condition that the molecule is not involved in any strong intermolecular interaction creating a marked anisotropy of the potential; in this case the axes of rotation coincide with the axes of the potential).

In general, rotation must be defined by three correlation times (relative to each of the three axes), but for molecules of the symmetric top type there are only two times, $\tau_{\parallel}$ and $\tau_{\perp}$ (rotation relative to the axis of highest order symmetry and about axes perpendicular to it).

The anisotropy of molecular rotation can be successfully studied using the NMR relaxation of nuclei exhibiting a quadrupole moment; it is necessary that the molecules contain not less than two nuclei which exhibit quadrupole moments and which do not lie on the same molecular axis[59] For example, for the CD_3CN molecule the rotational correlation time calculated from the rate of relaxation of ^{14}N nuclei describes the motion at right angles to the axis of symmetry of the molecule, since the gradient of the electric field inducing the relaxation of the nucleus is directed along the C≡N bond; this time is 1.2 ps. The time 0.14 ps, calculated from the rate of relaxation of the deuterium nucleui, characterises the rotation about all three axes, although the predominant contribution is made by the rotation about the axis of symmetry. Thus for CD_3CN at 25°C, $\tau_{\parallel} = 0.14$ ps, $\tau_{\perp} = 1.2$ ps. The activation energies of rotation about different axes are also different: $\epsilon_{\parallel} = 0.8$ kcal mole^{-1}, $\epsilon_{\perp} = 1.7$ kcal mole^{-1}.[59]

The pressure dependence of $\tau_{\parallel}$ and $\tau_{\perp}$ has been studied [60]; at 23°C, $\tau_{\parallel}$ is almost independent of pressure (up to 2 kbar), whereas $\tau_{\perp}$ increases by a factor of almost 3. The activation volumes are $V_{\parallel} \leq 2$ cm^3 mole^{-1} and $V_{\perp} = 8.5$ cm^3 mole^{-1}; these quantities have the significance of the fluctuations of the free volume required to unfreeze rotation. It is obvious that for rotation about a perpendicular axis it is necessary to create a fluctuation of a large volume, whereas rotation about an axis of symmetry requires almost no additional volume. These results agree with the theoretical models of rotation previously examined.

A similar relationship has been found for CD_3I (at 23°C, $V_{\parallel} < 2$ cm^3 mole^{-1}, $V_{\perp} = 10.0$ cm^3 mole^{-1}), and for toluene and other molecules [31]. The rates of relaxation of the quadrupolar nuclei D and ^{35}Cl have been used to determine $\tau_{\parallel}$ and $\tau_{\perp}$ for $CDCl_3$;[59] at 20°C the values are 1 ps and 2 ps, and the activation energies are 0.8 kcal mole^{-1} and 1.6 kcal mole^{-1} respectively.

For BCl_3, the ratio $\tau_{\perp}/\tau_{\parallel} \simeq 0.75$, and for $VOCl_3$ and CCl_3CN these ratios are 1.4 and 2 respectively (20°C); for pyridine, the value of $\tau_{\perp}/\tau_{\parallel}$ changes considerably with temperature (it is equal to 3 at −20°C and 1 at 90°C).[61] The anisotropy of the rotation of the nitroxide radicals used as spin markers and probes is of considerable interest. The anisotropy of their rotation was first studied by Vasserman and coworkers[62]. The rotation of the radical $(SO_3)_2^{2-}NO$ is anisotropic[49,51,62]: it is most rapid about the axis perpendicular to the N–O bond and the $2p\pi$-orbital of the unpaired electron; the ratio of the frequencies of rotation in water and in glycerol has the values 2.9 and 4.7. The anisotropy of the rotation depends on temperature only for small radicals[51]. The temperature dependence of the anisotropy of rotation is an important characteristic: its existence indicates that the anisotropy of the rotation is due to the anisotropy of the force potential, and its non-existence indicates that the rotational anisotropy is due to the anisotropy of the moment of inertia.

For benzene, toluene, nitrobenzene, and mesitylene, the correlation times $\tau_{\parallel}$ and $\tau_{\perp}$ obey Eqn.(5), but the dependence of these times on the viscosity is strongly anisotropic, that is the proportionality coefficients $C_{\parallel}$ and $C_{\perp}$ differ considerably[63]. This indicates that the simple hydrodynamic model is unsuitable for the description of the mechanism of the elementary movements.

6. Molecular Rotation Frequency Scales

The molecular movements of highest frequency in a liquid are those movements which lead to a change in the moment of inertia; their characteristic times τ_J are of the order of 10^{-13} s or less, and coincide with the times obtained from an analysis of the far edge of the Rayleigh scattering line[64]. If the liquid is regarded as a quasi-crystalline solid, this time can be identified with the period of the oscillations in the lattice sites.

The rotational reorientations of molecules take place much more slowly (see Table 2); even small and symmetrical molecules undergo reorientations in times of ~2–10 ps, and the rotation of large and unsymmetrical molecules in viscous solvents takes place in times of 10^{-10}–10^{-9} s.

Table 2. Rotational correlation times of various molecules in liquids.

Molecule	°C	τ_0, ps	Refs.
HF	25	0.8	65
CS_2	20	2	66
C_6H_6	20	4	61
Cyclopentane	20	1.3	67
ClO_2F	−143÷95	0.06 exp (900 RT)	58
F_2	−217	6.8	65
Bromobenzene	23	13	64
Nitrobenzene	25	32	66
Toluene	20	14	64
m-Nitrotoluene	23	44	64
Rhodamine 6G in octanol	20	1600	68
Rhodamine 6G in $CHCl_3$	20	100	68
Bengal Pink in CH_3OH	20	180	69
Bengal Pink in iso-C_3H_7OH	20	890	69
Eosin in water	20	550	69
Macromolecules (mol.mass ~10^6)	20	~10^8	–

The activation energies of rotation for small and symmetrical molecules are 1–3 kcal mole^{-1}, and for large and anisotropic molecules they may reach 5–7 kcal mole^{-1} and sometimes more. An interesting feature is that the pre-exponential factors for the rotational correlation times amount to ~10^{-13} s and coincide with τ_J.

New possibilities for the study of quantitative dynamics were opened up by picosecond spectroscopy (the data for dyes given at the end of Table 2 were obtained by direct observation of the depolarisation of the fluorescence by picosecond spectroscopy).

The phenomenon of optically induced birefringence (optically induced Kerr effect) is of particular interest. The electric field of a powerful laser pulse passing through the liquid brings about partial orientation of electrically anisotropic molecules. After the passage of the light pulse, the system exhibits the property of birefringence, which disappears with a characteristic time τ_θ. The action of super-fast shutters (Kerr cells) is based on this phenomenon.

III. DYNAMICS OF TRANSLATIONAL MOTION

A macroscopic characteristic of translational dynamics is the diffusion coefficient

$$D_t = \frac{\langle l^2 \rangle}{6\tau}, \qquad (16)$$

where τ is the time in which a particle, on the average, is displaced through a distance l. A familiar expression is the Stokes–Einstein relationship

$$D_t = \frac{kT}{6\pi a\eta}, \qquad (17)$$

which is obtained from the hydrodynamic equations for the movement of a sphere of radius a in a continuous medium with a viscosity η. As in the case of rotational diffusion, this macroscopic description is inadequate; the experimental values of D_t are usually greater than the predicted values, particularly in viscous liquids, polymer solutions, etc. In order to adapt Eqn.(17) for the description of the experimental results, the concept of the micro-viscosity η^* ($\eta^* = f_t\eta$) was introduced [32], with micro-viscosity coefficient

$$f_t = 0.16 + 0.4\,(a/a_L), \qquad (18)$$

where a_L is the radius of the molecules of the solvent. With this correction, Eqn.(17) in most cases reproduces the experimental results satisfactorily (to within 20–30%).

Strictly speaking, Eqn.(17) is not applicable for the description of the micro-dynamics of diffusion. It is often used, however, with the assumption that $\langle l^2 \rangle \simeq \langle a^2 \rangle$ and $\tau = \tau_t$, where τ_t is the time corresponding to a displacement through a distance of the order of the molecular diameter. The particle can cover this distance either by continuous Brownian movement or by abrupt movements.

Existing theories of the molecular mechanism of translational movements are based on the concepts of fluctuations of the free volume and their migration, and in fact represent a development of Frenkel's ideas [70]. The theories predict the Arrhenius temperature dependence of the diffusion coefficient $D = D_0 \exp(-\epsilon_D/RT)$ with ϵ_D close to the activation energy of viscous flow. For some atoms and molecules (of the type Ar, O_2, etc.), however, diffusion takes place without activation, and the diffusion coefficient is proportional to temperature and independent of viscosity [71]. The Arrhenius relationship usually applies in a narrow temperature range; the study of diffusion over a wide temperature range shows that ϵ_D itself depends on temperature. The activation volume of diffusion (which is obtained from the pressure dependence of D) also is not constant and depends on temperature [31]. This indicates that translational molecular movement is not an elementary process, and although different theories give different aspects of this process satisfactorily, there is no complete rigorous theory of both rotational and translational diffusion.

The most extensive information on translational dynamics is obtained by measuring the magnetic relaxation of nuclei and electrons (NMR and EPR). The diffusion coefficients are determined by the spin echo method; the correlation time τ_t and the amplitude of the translational displacement are calculated from the intermolecular dipole contribution to the relaxation of the nuclei (in NMR) or electrons (in EPR).

An example is provided by data [72] on the relaxation times of the protons of chloroform diluted with deuterochloroform. The relaxation time depends on the diffusion coefficient, the distance of closest approach of the nuclei when the molecules come into contact, and the amplitude of the displacement. If the approach distance is taken as 4.1 Å (from molecular models), the amplitude of the displacement is found to be 4.6–5.5 Å. On the other hand, if it is assumed that diffusion takes place by a Brownian mechanism, that is if it is assumed that the amplitude of the displacement is infinitely small, the approach distance is 2.3 Å, which is a physically unrealistic value. From this it may be concluded that translation in chloroform takes place by abrupt movements, with an amplitude of 4.6 to 5.5 Å.

The correlation time τ_t is calculated from the experimentally determined diffusion coefficients using Eqn.(16), where l = 4.6–5.5 Å:

$$\tau_t = 4 \cdot 10^{-13} \exp(-2300/RT).$$

The pre-exponential factor is close to the value of τ_J, and characterises the period of the vibrations of the molecule in the equilibrium position. In liquid HF at 25°C, it was found that $D = 10^{-4}$ cm^2 s^{-1}, τ_t = 2.3 ps (from NMR data) or 4.0 ps (from neutron scattering); the amplitude l = 3.7 Å (NMR) or ~5 Å (neutron scattering) [65]. For cyclopentane and cyclohexane at 20°C, the amplitudes of the rotations, calculated from the scattered neutron spectra, are 0.3–0.6 Å (the displacement of a point along the surface of the sphere of rotation); the amplitudes of the vibration of the centre of gravity of the molecules are 1.3–1.9 Å in the temperature range from the melting point to the boiling point [67].

The quasi-elastic scattering of cold (low-energy) neutrons is becoming a powerful experimental method for studying the molecular dynamics of liquids. The energy spectrum of scattered neutrons gives the frequency spectrum of the atomic–molecular movements with characteristic times 10^{-4}–10^{-11} s and amplitudes of the atomic–molecular displacements 0.1–10 Å.

Neutron scattering data show that both the orientational and the translational movements contain as components displacements of both small amplitude and large amplitude. Their relative proportions depend on the shape of the molecules, temperature, and the viscosity of the liquid.

In recent years, fairly exact mathematical methods have been developed for calculating the coefficients of rotational and translational diffusion. These methods are based on the view of a liquid as a system of close-packed rigid spherical (or almost spherical) particles. These

ideas effectively give the static structure of a liquid. It is assumed[73] that they can also be used to describe its dynamics. A dynamic theory has been developed[74], based on the fact that single-particle movement in a liquid is controlled by the forces of intermolecular repulsion (the steep branch of the intermolecular potential). The dynamics of this system are close to the dynamics of a system of rigid particles[74]. It is assumed that the long-range (changing slowly with distance) intermolecular forces can be neglected. This approximation is applicable to the description of single-particle movement, but is naturally inapplicable to the examination of the collective correlated movement of several particles (for example in liquid crystals).

Thus the one-particle approximation works satisfactorily, and makes it possible to calculate the coefficients of rotational and translational diffusion with good accuracy.

Direct proof that the dynamic processes in a liquid are controlled by short-range forces of repulsion has been obtained[75] by calculating the correlation functions for the velocity of particles in a model liquid, in one case taking account of the entire intermolecular Lennard–Jones potential, and in the second case taking account of only its repulsive part; the correlation functions were found to be the same in both cases.

The same method (computer modelling of the dynamic processes) showed that the diffusion coefficients in a model liquid consisting of rigid spheres coincides to within 10 units with the diffusion coefficients in a liquid in which the entire Lennard–Jones potential is taken into account, that is long-range forces of attraction do not play a significant role in the molecular dynamics of a liquid, although these forces play a decisive role in the thermodynamics of liquids.

IV. MOLECULAR DYNAMICS OF PAIRS

All bimolecular chemical and physicochemical processes take place in pairs of interacting particles (chemical reactions, energy transfer, quenching of excited states, complex formation, etc.); the probability that a process will take place in a single encounter of the reacting particles is determined to a considerable extent by the dynamics of the pair. These dynamics can be examined for the case of a pair of radicals; this reproduces all the characteristic features of the behaviour of any molecular pair of uncharged particles.

A radical pair is a dynamic system in which the partners may diffuse into the volume, move apart, and return again to the original pair, undergoing diffusion journeys along random trajectories of different length and duration. The probability of return gradually decreases with increase in the length of the trajectory; this probability will be defined by a function $f(t)$. In other words, $f(t)$ is a function of the distribution of the pairs with respect to lifetime, that is the probability that a pair survives to the instant of time t; this means that the partners leaving a pair at the instant $t = 0$ return again to the pair at the instant t with a probability $f(t)$.

The probability of reaction in a pair (for example recombination) consists of two terms:

$$P = \varepsilon + (1-\varepsilon)\int_0^\infty \varepsilon f(t)\,dt\,. \qquad (19)$$

The first term takes account of primary recombination, which has a probability ϵ; it is due to the "collapse" of those pairs in which the radicals have been unable to move apart before the instant t. The second term expresses the probability of secondary recombination, due to the repeat encounters of radicals which have left the pair at the instant $t = 0$ and returned to it at the instant t.

From the theory of the random diffusion of particles in a liquid[77], the following expression was proposed for the function $f(t)$:

$$f(t) = mt^{-3/2}\exp\left(-\frac{\pi m^2}{p^2 t}\right), \qquad (20)$$

where $p = \int_0^\infty f(t)dt$ is the probability that the pair undergoes at least one secondary encounter ($1 - p$ is the probability that the radicals never return to the original pair); usually, $1/2 < p < 1$. The values of p and m are determined by the following expressions[78]:

$$p \simeq 1 - (1/2 + 3\rho/2\sigma)^{-1}$$
$$m = 1.036\,(1-p^2)\,(\rho/\sigma)^2\,\nu^{-1/2},$$

where ρ is the diameter of the contact pair, σ the step of the mean-square diffusion displacement of the radicals ($\sigma^2 = 6D\nu^{-1}$), and ν the frequency of the diffusion displacements.

The function $f(t)$ in the form of Eqn. (20) describes the molecular dynamics of any pair of neutral particles. Substituting Eqn. (20) in Eqn. (19) gives the probability of reaction in the pair:

$$P = \varepsilon + \varepsilon\,(1-\varepsilon)\,p^{*}. \qquad (21)$$

This equation in fact determines the magnitude of the cage effect. It is applicable with the condition that the lifetime of the isolated radicals is infinite. In fact, the radicals have a finite lifetime: within the diffusion time they may be transformed into other radicals (by decomposition, isomerisation, or replacement). As a result, chemical dynamics are superimposed on the diffusion dynamics of the pair; the function $f(t)$ must be modified in such a way that it takes account of the diffusion trajectories and return of only the surviving radicals. If the rate constant of the chemical transformation is k, the probability of "survivial" of the radicals until time t in the pair is equal to $\exp(-kt)$; the dynamics of a pair of surviving radicals are then described by the function

$$\varphi(t) = f(t)\exp(-kt). \qquad (22)$$

This function describes the dynamics of any pair of particles having a finite lifetime $\tau = k^{-1}$; for processes involving the bimolecular quenching or transfer of energy (vibrational or electronic), k is the rate constant of the radiative or non-radiative unimolecular deactivation of the excited particle. For processes involving radicals, the function (22) describes the dynamics of not only chemical but also physical transformations (inversion, rotation, *cis-trans* isomerisation); it can then be used to calculate the degree of preservation of the stereochemical configuration or optical activity in the product formed.

Substituting the function $\varphi(t)$ in Eqn. (19) in place of $f(t)$ gives

$$P = \varepsilon + \varepsilon\,(1-\varepsilon)\,p\cdot\exp\left[-(2m/p)\sqrt{\pi k}\right]. \qquad (23)$$

For processes involving the recombination of radicals, P is the probability of formation of the product in the radical pair, and ϵ the probability of recombination in each contact of the partner. For preservation of the stereochemical configuration, P is the probability of preservation,

and k the frequency of the inversion or spatial reorientation of the particles in the diffusion journeys. For processes involving excited particles, P is the probability of the quenching or transfer of energy in the pair formed by the excited molecule and the quenching agent (or energy acceptor), and ϵ the probability of this process in each contact of the partners.

The dynamics of radical pairs exhibits another remarkable feature: in addition to diffusion and chemical dynamics, it exhibits spin dynamics, that is the dynamics of the evolution of spin states, or singlet–triplet transitions. Spin dynamics are controlled by the magnetic interactions in the radicals and depend on the difference in the Zeeman energies of the radicals (and hence on the external magnetic field intensity), the energy of the hyperfine electron–nuclear interaction, and the magnitude of nuclear spin of the radicals. This leads to magnetic effects in radical reactions, the importance of which was understood and evaluated only in recent years [79,81]. These include the chemical polarisation of nuclei and electrons, the magnetic isotope effect, and the influence of a magnetic field on chemical reactions [80]; a complete review of studies in this field has been published [82].

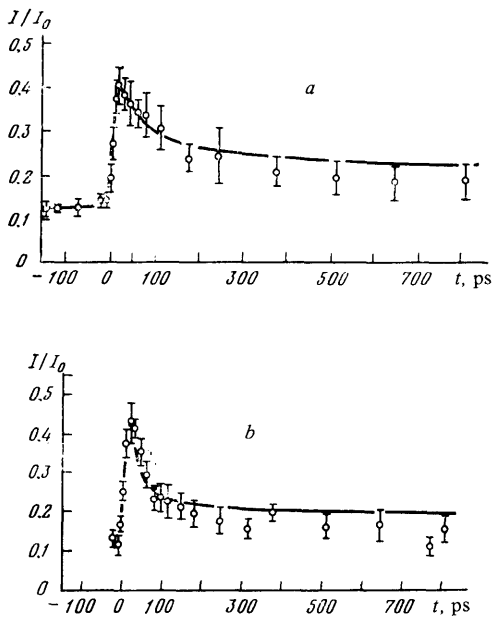


Figure 4. Kinetics of the cage recombination of iodine atoms: *a*) in CCl_4; *b*) in hexadecane [84]. The points give the experimental results, and the lines the results of the calculation using the Noyes model; the moment $t = 0$ corresponds to the end of the exciting pulse.

The dynamics of molecular pairs of free uncharged particles has been discussed; its experimental verification can now be examined.

Firstly, quantitative studies of magnetic effects (in particular, the chemical polarisation of nuclei) have shown that the function $\varphi(t)$ in the form of Eqn.(22) effectively describes the experimental results. The polarisation of nuclei takes place in a pair as a result of singlet–triplet transitions with a characteristic time of $10^{-8}-10^{-10}$ s; the main contribution to the polarisation is therefore made by long diffusion trajectories, the duration of which is comparable with the time of singlet–triplet transitions. In other words, the main contribution to the polarisation of nuclei is made by diffusion displacements with a duration $t \gg m^2/p^2 \simeq 10^{-12}-10^{-11}$ s. With this condition, the function $f(t)$ has the simple form

$$f(t) \simeq mt^{-3/2} \qquad (24)$$

and describes the large-scale diffusion dynamics of long-lived particles.

Secondly, computer calculations of the molecular dynamics of pairs (so-called machine experiments) have confirmed the general form of the function $f(t)$ given by Eqn.(20) and have shown that the probability of a secondary encounter of the particles in a pair decreases with time as $t^{-3/2}$, in agreement with Eqn.(24). [83]

Finally, direct confirmation of the form of the function $f(t)$ has been obtained by picosecond spectroscopy [84]. A solution of I_2 in CCl_4 and $C_{16}H_{34}$ was irradiated by a powerful 5300 Å laser pulse of duration ~5 ps. At this frequency, I_2 is excited into the state $^3\Pi_{0_u^+}$, from which collision-induced predissociation to two atoms in the state $^2P_{3/2}$ takes place. The iodine atoms recombine in the pair (in the cage) or move apart and recombine in diffusion encounters with other atoms, avoiding cage recombination. The formation of I_2 molecules from the atoms is detected by probe laser pulses which measure the transmission at a wavelength absorbed by I_2 (5300 Å); the results are shown in Fig. 4.

After the passage of the exciting pulse, the transmission of the solution at first increases as the I_2 molecules dissociate into atoms, and then decreases, when the iodine atoms begin to recombine, and reaches a stationary value after ~800 ps. The stationary value of the transmission does not coincide with the initial transmission; the difference corresponds to the number of iodine atoms which have avoided cage recombination and moved into the volume. Their recombination in the volume is limited by diffusion, and takes place in a time of $\sim 10^{-8}$ s. The fraction of atoms leaving the cage is 25% in CCl_4, and 5% in hexadecane [84].

The characteristic time of the cage recombination of iodine atoms is ~140 ps in CCl_4, and ~70 ps in hexadecane [84]; this time can in fact be regarded as the lifetime of the cage in the liquid. The kinetics of the recombination are described satisfactorily by Eqn.(20); the best agreement between theory and experiment is obtained for the following values of the parameters: frequency of the abrupt diffusion movements $(1-5) \times 10^{12}$ s^{-1} in CCl_4 and $(2-20) \times 10^{12}$ s^{-1} in $C_{16}H_{34}$; amplitude of the elementary diffusion displacement 0.5–1.0 Å in CCl_4 and ~0.1 Å in $C_{16}H_{34}$. [84] These values are of course approximate, but they give the correct order of magnitude and are physically reasonable.

The function $f(t)$ characterising the dynamics of pairs of oppositely charged particles should describe the diffusion movement of the particles in the Coulombic field of mutual attraction. The problem of the behaviour of a

pair of this kind has been solved in radiation chemistry [85,88], where it is necessary to calculate the probability of the return of a thermalised electron or negative ion to the original positive ion.

Finally, mention may be made of the dynamics of combined pairs, in which the interacting centres are joined by a chain of atoms and chemical bonds. The dynamics of pairs of this kind represents essentially conformational and not diffusion dynamics. If however the connecting chain is sufficiently long, diffusion will influence the rate of the conformational transitions. An example of systems of this kind is provided by nitroxide biradicals, in which two paramagnetic nitroxide fragments are joined in a single molecular system [47]. The exchange interaction of the unpaired electrons in these biradicals takes place chiefly in intramolecular collisions of the paramagnetic centres, so that it depends on the flexibility of the connecting bridges, the number of chemical bonds, and the solvent[87]. The encounter frequency and rate of spin exchange are controlled by the conformational dynamics of the connecting bridge.

A study of the frequency of the intramolecular transfer of an electron between two α-naphthyl groups joined by a polymethylene chain [88] showed that the frequency of transfer decreases according to the law $(n+1)^{3/2}$ for $n \geq 6$ (n is the number of methylene groups in the chain). The activation energy of transfer is small, and independent of n.

The disproportionation of the biradicals

$$\dot{C}H_2-(CH_2)_n-\dot{C}O \rightarrow CH_2=CH-(CH_2)_{n-1}-C\overset{O}{\underset{H}{\diagup\!\!\diagdown}}$$
$$(n = 7-11)$$

is an intramolecular process; the disproportionation product is found to show polarisation of the nuclei, which depends on the magnetic field intensity [80]. The polarisation is produced as a result of $S-T_{-1}$ transitions in the biradical at the moments at which the ends of the biradical, in their random movement, pass through a position in which the condition $2J \simeq g\beta H_0$ is satisfied (when the exchange energy of the electrons is equal to the Zeeman energy). In this position, the energy levels of the singlet (S) and one of the triplet (T_{-1}) states intersect; the magnitude of the polarisation depends on the frequency with which the system passes through this point.

Quantitative calculations of the nuclear polarisation [90] have shown that the probability of passage through the point of intersection of these levels is given satisfactorily by the Treloar function for a freely connected chain.

In both of these examples, the molecular dynamics of the combined pairs is controlled chiefly by the conformational dynamics of the connecting bridges.

V. DYNAMICS OF VAN DER WAALS MOLECULES

Van der Waals molecules (VM) are weakly bonded complexes of atoms, radicals, or molecules, which exist as a result of intermolecular attraction. Dimers of the atoms of the inert gases (Ne_2, Ar_2, Kr_2, Xe_2), and also the complexes $Ne-H_2$, $Ar-H_2$, $Kr-H_2$, $Xe-H_2$, $Ar-N_2$, $Ar-O_2$, $Ar-HF$, $(H_2)_2$, $(O_2)_2$, H_2-N_2, $(NO)_2$, $(CO_2)_2$, etc., are known and have been extensively studied. The properties of VM have been reviewed [91]. Van der Waals molecules have characteristic vibrational–rotational spectra and are detected by infrared and microwave spectroscopy, in experiments on molecular scattering, and in molecular beams.

The main contribution to the energy of formation of VM is made by dispersion interaction (equilibrium distances 3.5–4.5 Å). The dissociation energies of VM are comparable with their kinetic thermal energy and amount to 0.2–0.9 kcal mole^{-1}, so that almost every collision with a foreign molecule leads to decomposition of the VM. At room temperature and a pressure of 1 atm, the time between molecular collisions is $\sim 10^{-10}$ s; the lifetime of the VM is approximately the same. Decrease in temperature increases the lifetime and concentration of VM, and increase in pressure decreases the VM lifetime.

The formation of VM is revealed in the macro-properties of gases, changing the form of the $p-V-T$ diagram, the magnitude of the second virial coefficient, the viscosity, etc. It is assumed [91] that VM take part in processes involving the transfer of its energy, translational–rotational exchange, the spin–rotational relaxation of electronic spin in quantum generators with optical pumping. In addition, VM induce processes of gas condensation; it is suggested [91] that various gaseous chemical reactions may take place with the participation of VM; these reactions may have a negative temperature coefficient (for example the oxidation of NO).

An interesting role is played by VM in reactions taking place in molecular beams. The angular distribution of the reaction products indicates unambiguously that many reactions include the formation of an intermediate complex, the lifetime of which is greater than or comparable to the period of rotation of the complex ($\tau \geq 10^{-12}$ s).[92] This lifetime is much greater than the duration of the collision of the reagent molecules. These reactions include: $Cs + RbCl \rightarrow CsCl + Rb$; $Cl + BrI \rightarrow ClBr + I$; $Cl + I_2 \rightarrow ClI + I$; $D + H_2 \rightarrow DH + H$, etc.[92] The intermediate complexes in these reactions can be regarded as VM, since they can hardly involve any specific interaction other than van der Waals interaction (for example the complex D–H–H, which precedes the reaction $D + H_2 \rightarrow DH + H$).

VM must undoubtedly also exist in a liquid, although their lifetime, other conditions being equal, should be shorter than in the gaseous phase. It is possible to detect VM from the increase in the correlation time of rotational motion in a liquid; the measured time is a complex function of the reorientation time of single molecules and their pairs [93]. This is revealed experimentally by an increase in the rotational correlation time of the molecules with increase in their concentration (at constant viscosity).

These effects are usually investigated by studying the dependence of τ_θ on viscosity at different concentrations of the molecules. The $\tau_\theta(\eta)$ relationship obeys Eqn. (5) at all concentrations, but at η = const. the time τ_θ is greater at higher concentrations of the molecules, that is for a greater contribution of pairs to the measured light scattering. An increase is shown not only by the values of τ_θ but also by their values extrapolated to $\eta = 0$, which are close to the periods of rotation of free rotators in the gaseous phase. This effect has been observed for solutions of benzene, toluene, nitrobenzene, perfluorobenzene, and chloroform [30,40]. Thus for nitrobenzene in an infinitely dilute solution in CCl_4 the time τ_θ is 2.4 ps, and reaches 5.6 ps with increase in the concentration of nitrobenzene to 50% (at the same viscosity). It was concluded that the nitrobenzene molecules are "joined" in pairs in such a way that their planes are arranged in parallel [93]. The pairs of benzene molecules are "joined" with their planes at right angles; the same relative orientation of neighbouring molecules is observed in solid and liquid benzene (from X-ray scattering data [94]). The recently

detected[94] dimers of benzene in the gaseous phase apparently have the same structure, since they exhibit a dipole moment.

The dimers of molecules are short-lived species; their lifetime τ is shorter than the period of rotational reorientation in the liquid τ_θ, but greater than the period of free rotation in the gaseous phase, and amounts to several picoseconds. Thus the dimers can be regarded as van der Waals molecules. The depolarisation of the Rayleigh light scattering in benzene + perfluorobenzene and perfluorobenzene + mesitylene mixtures has revealed pairs of these molecules[95]: the value of τ_θ for the mixtures is 2–4 times τ_θ for the isolated molecules (at a constant viscosity in the same inert solvent, for example in CCl_4). In this case also, the molecular pairs can be regarded as VM with a lifetime $\tau \lesssim \tau_\theta$.

As noted earlier, Rayleigh scattering is observed in solutions of optically anisotropic molecules in optically isotropic solvents. The molecules of these solvents are symmetrical and do not exhibit anisotropy of the polarisability (for example CCl_4). In molecular collisions, however, the electronic structure of the interacting particles changes, with a consequent breakdown of the symmetry of the electron cloud and the production of short-lived fluctuations in the anisotropy of the polarisability. For this reason, symmetrical molecules (and even atoms) also show Rayleigh scattering; the line corresponding to this scattering is usually very broad, and is superimposed on the narrow line corresponding to the ordinary Rayleigh scattering of optically anisotropic molecules.

Rayleigh scattering induced by collisions has been observed in gases (He, Ne, Ar, Xe, H_2); it has been shown that it is due to van der Waals molecules $(He)_2$, $(Ne)_2$, etc.[91] The same scattering has been observed in liquids (Xe, Ar, $SnBr_4$, CCl_4); the correlation times of the paired interactions inducing the Rayleigh scattering amount to 1–3 ps.[96] These times are obviously too long to be regarded as the duration of the collision. In a liquid, the light scattering is most probably due to VM, in which the anisotropy of the optical polarisability is revealed; the lifetime of these VM is ~1–3 ps and is shorter than the period of rotational reorientation.

The problem of possible complex formation by the most important chemical reagent—molecular oxygen—is of particular interest. Evans[97] was the first to observe singlet–triplet absorption by benzene in the presence of oxygen; it was assumed that oxygen removes the spin-forbidden character of the singlet–triplet transition in benzene, and hence interacts somehow with the electron cloud of the benzene molecule. It was later found[98] that in the presence of oxygen, new absorption bands appear in the electronic spectra of hydrocarbons, alcohols, and aromatic molecules; they were assigned to charge-transfer complexes. The equilibrium constants for complex formation were small, however, and the bond energies $\lesssim$300 cal mole^{-1}. The results were often contradictory and indefinite; the formation of the complex $C_6H_6 + (O_2)_2$ was also suggested[98]. A displacement of the $^1\Sigma_g^+ \longleftrightarrow {}^3\Sigma_g^-$ absorption band of molecular oxygen from 760 nm (in the gas) to 630 nm (in water) is also observed[99]. All these facts have been regarded as signs of the interaction of the electron clouds of molecular oxygen and organic molecules.

Convincing proof of this interaction was obtained by NMR: in the presence of molecular oxygen, dissolved under a pressure of 3–50 atm in the liquid, the NMR lines of most molecules studied (water, alcohols, dioxan, amines, acetone, cyclohexene, phenylacetylene, chloroform, benzene and its derivatives, anthracene, etc.) undergo paramagnetic shifts and broadening[100,101]. The paramagnetic shifts show unambiguously that in the interaction of the oxygen molecule with dissolved molecules, overlap of their electron clouds and partial transfer of the unpaired electrons of oxygen to the organic molecules take place.

This "collectivisation" of electrons can be regarded as a sign of the participation of oxygen in a complex, but the equilibrium constants of complex formation are very small and do not exceed 10^{-2} litre mole^{-1}.[101] The bond energies in the complex are also small, and different for different groups of a given molecule. Thus the bond energy measured from the temperature dependence of the paramagnetic shift of the protons of the CH_3 group in toluene is 1.7 kcal mole^{-1}, whereas that measured from the protons of the aromatic ring is close to zero; in methanol, the bond energy measured from the protons of the CH_3 group is close to zero, whereas that measured from the hydroxyl protons is 0.5 kcal mole^{-1}.[101] Thus different fragments of the same molecule interact in different ways with oxygen.

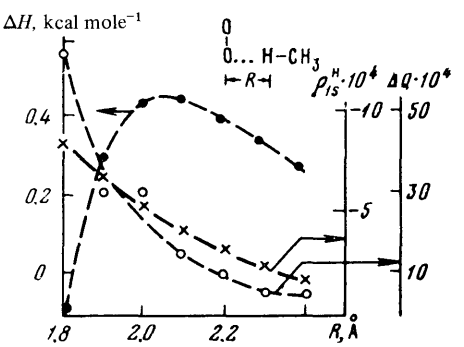


Figure 5. Dependence of ΔH, ρ^H_{1S}, and ΔQ on the distance between the partners of the complex $O_2 \ldots CH_4$.

In binary or ternary mixtures, the paramagnetic shifts depend little or not at all on the composition of the mixtures; this means that there is practically no competition between different molecules for a position in the coordination sphere of oxygen[101]. All these facts show that oxygen forms very weak complexes, which must be regarded as van der Waals molecules. Some results of a quantum-chemical calculation of the most stable configuration of the system $O_2 + CH_4$ are given in Fig. 5; the calculated equilibrium distance is ~2.05 Å, the bond energy $\Delta H \simeq 400$ cal mole^{-1}; the charge ΔQ transferred from oxygen to the methane molecule is $\sim 2 \times 10^{-3}$; the spin density ρH_S on the hydrogen atom attached to the p_z orbital of oxygen is $\sim 3 \times 10^{-4}$. The calculated values of the bond energy and the transferred spin density are close to the experimental values.

The equilibrium constant (~10^{-2} litre mole^{-1}) can be used to estimate the lifetime of VM involving oxygen: the value is ~10^{-12} s. The paramagnetic broadening of NMR lines is completely determined by the intermolecular contribution[101]; the intramolecular contribution, due to the dipole electron–nuclear interaction within the VM, is

negligible. This means that the lifetime of the VM is shorter than the period of its rotational reorientation, that is $\tau \leqslant (1-5) \times 10^{-12}$ s.

In general it should be noted that it is almost impossible to distinguish a distinct boundary between van der Waals molecules and weak short-lived complexes. Neither the lifetime nor the bond energy nor even the transfer of spin (electron) density can serve as unambiguous criterion of the difference between these particles. The only difference between a complex and a VM is the nature of the forces holding the partners in the complex or in the van der Waals molecule; it is fairly difficult, however, to detect this difference experimentally. The partners in VM are held by van der Waals (mainly dispersion) forces; in contrast to the case of the forces responsible for specific interactions in a complex, it should be impossible to saturate dispersion forces; in other words, the coordination number for VM may be large (up to 4–6). It is impossible in practice, however, to reach the concentration range in which this characteristic feature of VM might be detected.

VI. PROCESSES OF COMPLEX FORMATION AND SOLVATION

Complex formation by particles is generally accompanied by the partial overlap of the electron clouds of the partners, which changes the reactivity of the particles in the complex. In the study of complex formation by organic molecules in a liquid, the following principal problems arise: what types of complex exist, what orbitals are used by the partners for complex formation, in what combinations are these orbitals used, how are the orbitals oriented in space, what are the interatomic distances in the complexes, and what are the lifetimes of the complexes? Extensive information on complexes has been obtained by the classical methods of optical spectroscopy, NMR, and dielectric measurements [102]. In recent years, NMR studies of paramagnetic complexes of the type $\dot{R}\ldots L$ (where $\dot{R}$ is an organic radical, and L an organic ligand molecule) [47] have revealed a number of important regular features of complex formation. An advantage of complexes of the type $\dot{R}\ldots L$ is that they have an unpaired electron, which is situated in collectivised molecular orbitals of the complexes. The unpaired electron is transferred with a definite probability (measured by NMR) to the ligand atoms, and reflects all the interactions taking place in the complex.

The theory of the paramagnetic shifts and broadening of the NMR lines in paramagnetic complexes has been developed, the dependence of these spectral changes on the concentration of the complexes in the solution studied, and an approach to the extraction of information on the structure and dynamics of these complexes formulated [103-105]. The basic idea behind this approach is to organise competition between different ligand molecules for the orbitals of the radical. Thus for example the paramagnetic fragment of a nitroxide radical (Fig. 6) uses its π- and n-orbitals for complex formation with the ligand. If the solution contains two types of ligand, one of which reacts using the π-orbital while the other reacts using the n-orbital, the paramagnetic shifts of each of these ligands will be independent of the concentration of the other. Each ligand may add on independently to different orbitals of the radical, forming a two-coordinated complex. In this case there is no competition between the ligands for the orbitals of the radical. On the other hand, if both ligands add on to the same orbital of the radical forming complexes of the same type, the mole fractions of the complexes with each of these ligands (and hence their paramagnetic shifts) will depend on the concentration of the corresponding ligand. In this case the ligands compete for the same orbital of the radical.

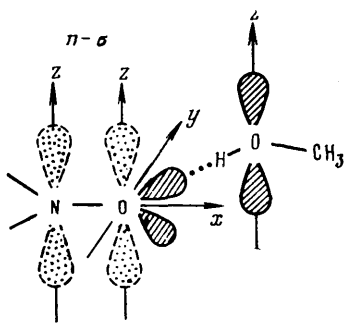


Figure 6. Participation of the orbitals of the paramagnetic fragment of a nitroxide radical in the formation of $n-\sigma$ complexes.

Table 3. Ligands competing with solvent molecules for the orbitals of a radical [105].

Ligand	Functional group (atoms to which the NMR signal relates)	Solvent	Type of complex	K, litre mole^{-1}	ρ_{1s}^{H} or ρ_{2s}^{13C}*
H_2O	OH (protons)	C_6H_5OH	$n-\sigma$	0.7	$1\cdot10^{-3}$
$CHCl_3$	CH (protons)	CH_3OH	$n-\sigma$	0.6	$0.8\cdot10^{-3}$
$(CH_3)_3CNH_2$	NH_2 (protons)	CH_3OH	$n-\sigma$	—	—
	CH_3 (^{13}C)	C_6H_{12}	$\pi-\sigma$	0.1	$1.3\cdot10^{-4}$
CCl_4	CCl (^{13}C)	C_6H_{12}	$\pi-n$	0.5	$1.8\cdot10^{-3}$
C_6H_{12}	CH_2 (^{13}C)	CCl_4	$\pi-\sigma$	0.05	$2.6\cdot10^{-4}$
$H_3CCH_2CH_2-C$ ‖ $H_3CCH_2CH_2-C$	CH_3, CH_2 (^{13}C)	C_6H_{12}	$\pi-\sigma$	—	—

*ρ_{1s}^{H} is the spin density in the 1s orbital of the hydrogen atom forming the hydrogen bond; ρ_{2s}^{13C} is the spin density in the 2s orbital of the carbon atom.

This principle has been widely used to determine the structures of the complexes of nitroxide radicals [105]; the chief results of the experimental studies are summarised in Tables 3 and 4.

Molecules containing hydroxyl or amino-groups form complexes of the $n-\sigma$ type; in these, the radical provides a n-orbital, to which the σ-bond O–H (or N–H) of the ligand is attached (see Fig. 6). These are ordinary hydrogen-bonded complexes; the ligands forming the hydrogen bond (H_2O, alcohols, amines, chloroform, organic acids, etc.) compete with one another for the n-orbital of the radical (Table 3). The hydrogen bond joins the radical and the ligand with the formation of a single quasi-π-system, in which ~1% of the density of the unpaired electron is transferred to the π-orbital of the ligand; this spin density subsequently extends to the ligand atoms by a

hyperconjugation or spin polarisation mechanism, leading to the appearance of spin density of different sign in the σ-electronic system of the ligand[106]. Various properties of complexes of radicals with a hydrogen bond are given in Table 5.

Table 4. Ligands not competing with solvent molecules for the orbitals of a radical[105].

Ligand	Functional group (atoms to which the NMR signal relates)	Solvent	Type of complex	K, litre mole^{-1}	ρ_{1s}^{H*}
CH_3OH	OH (protons)	CCl_4, C_6H_{12}	$n-\sigma$	3	$1\cdot10^{-3}$
C_2H_5OH	OH (protons)	CCl_4, C_6H_{12}	$n-\sigma$	0.7	$0.7\cdot10^{-3}$
$(CH_3)_3CNH_2$	NH_2 (protons)	C_6H_{12}	$n-\sigma$	—	—
$CHCl_3$	CH (protons)	CCl_4	$n-\sigma$	0.6	$0.8\cdot10^{-3}$
$C_6H_5OCH_3$	CH_3 (^{13}C)	CH_3OH	$\pi-\sigma$	—	—

*See footnote to Table 3.

Table 5. Equilibrium constants K, lifetimes τ_l, distances $r_{O\ldots H}$, and spin densities ρ_{1S}^{H} on the hydrogen atoms in complexes.

Ligand	K, litre mole^{-1}	τ_l, s	$r_{O\ldots H}$, Å	$\rho_{1S}^{H}\cdot10^3$
CH_3OH	3.5	$4\cdot10^{-11}$	1.75	−9.6
$CHCl_3$	0.6	$2.6\cdot10^{-11}$	1.77	−7.7
$C_6H_{11}OH$	—	$1.1\cdot10^{-10}$	1.45	−1.75
$(CH_2OH)_2$	—	$3\cdot10^{-11}$	1.74	−8.2

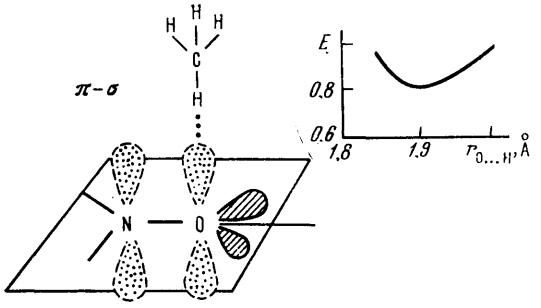


Figure 7. Molecular model of the $\pi-\sigma$ complex of methane and the potential energy curve for the complex; the spin density on the hydrogen atom of the ligand, attached to the π-orbital of the radical, is 3×10^{-4}, and that on the 2*s* orbital of the carbon atom is 1×10^{-3}.

Complexes of the $\pi-\sigma$ and $\pi-n$ type are of particular interest; they are formed using the π-orbital of the unpaired electron and the σ-bond C–H ($\pi-\sigma$ complexes) or with the participation of the unshared pairs of the ligands ($\pi-n$ complexes). The first are formed with saturated hydrocarbons using the CH_2 or CH_3 groups and are detected from the paramagnetic shifts of the ^{13}C nuclei[105]; a model of such a complex is shown in Fig. 7.

The $\pi-\sigma$ complex obviously lies on the reaction coordinate for the transfer of a hydrogen atom and precedes the activated complex, so that the distribution of the spin density and the mechanism of its propagation in $\pi-\sigma$ complexes is of theoretical interest.

Molecules forming complexes of the $\pi-n$ type compete with molecules forming $\pi-\sigma$ complexes for the π-orbital of the radical (see Tables 3 and 4). They do not compete, however, with molecules forming $n-\sigma$ complexes. The $\pi-\sigma$ and $\pi-n$ complexes are generally much less stable than the $n-\sigma$ complexes; their equilibrium constants and lifetimes are an order of magnitude smaller than those for $n-\sigma$ complexes. They are not van der Waals molecules, however, since their formation involves rigorously defined localised interactions: each partner provides its own particular orbitals, which exhibit regular relative orientations and arrangements.

If the molecule contains different functional groups, they may take part in the formation of different complexes. Thus t-butylamine gives a $n-\sigma$ complex involving the NH_2 group, and a $\pi-\sigma$ complex involving the CH_3 groups; $CHCl_3$ gives $n-\sigma$ and $\pi-n$ complexes involving the C–H and C–Cl bonds respectively; n-propylacetylene forms complexes of the $n-\sigma$ type (involving the acetylenic C–H bond) and of the $\pi-\sigma$ type (involving the CH_2 and CH_3 groups), etc. (see Tables 3 and 4).

It is comparatively simple to distinguish these complexes: $n-\sigma$ interaction generally leads to strong paramagnetic shifts on the protons, whereas $\pi-\sigma$ and $\pi-n$ interactions make a large contribution to the paramagnetic shift on carbon nuclei and a small contribution to the paramagnetic shift on protons. Aromatic molecules and alkene groups add on to radicals chiefly to give complexes of the $n-\sigma$ type (involving C–H bonds); interactions of the $\pi-\pi$ type are practically never observed, and apparently involve repulsion.

These regular features of complex formation have been confirmed for phenoxide and verdazyl radicals[107]; the complexes of nitroxide and phenoxide radicals with phenols have been extensively studied[108].

Complex formation by radicals changes the hyperfine interaction constants and the values of the g-factor[106]; this aspect is of particular importance when nitroxide radicals are used as spin tracers and probes. A situation is often realised in which a radical in two states—free and bound in a complex—has different frequencies of rotation and in addition is transferred from one state to another with a definite frequency. This dynamic problem has been solved[109]; the theoretical EPR spectra for different frequencies of exchange and rotation have been published[110].

Complex formation is also revealed in the rotational dynamics of molecules: the rotation about different axes is retarded indifferent ways, depending on how the molecules are attached to one another. Thus complex formation alters primarily the anisotropy of rotation. The rotation of the $CDCl_3$ molecule about the C_3 axis in benzene solution remains unchanged relative to the rotation in pure chloroform, but the rate of the rotation about the perpendicular axes is decreased by a factor of four[59]. This agrees with a structure of the complex in which the C–H bond of chloroform is adjacent and perpendicular to the plane of the benzene ring. In addition, the frequencies of the rotation of the molecules of benzene and chloroform in the complex about the common axis C_3-C_6 coincide,

that is the complex rotates as a whole, and there is no internal rotation about the C_3-C_6 axis[59].

The attachment of Ag^+, Na^+, or Li^+ ions to the CD_3CN molecule does not influence $D_\parallel$ but decreases $D_\perp$, that is the ions are attached to the CN group along the C_3 axis[59].

In conclusion, mention may be made of the measurement, by picosecond spectroscopy[111], of the characteristic time in which a free electron in water creates an equilibrium solvation layer, dropping into a potential well. This time is 4 ps, and corresponds to the rotational orientation time of dipolar molecules.

VII. INFLUENCE OF MOLECULAR DYNAMICS ON THE KINETICS OF CHEMICAL REACTIONS

The rate constant of a diffusion-controlled reaction k is equal to the product $k_{\text{diff}}P$, where k_{diff} is the rate constant of the encounters of the reacting particles, and P the probability of reaction in the pair. The quantity k_{diff} is determined entirely by the dynamics of the translational motion, and is usually estimated from the Smolukhovskii relationship[28]: $k_{\text{diff}} = 4\pi(r_A + r_B)(D_A + D_B)$, where r and D are the radii and diffusion coefficients of the interacting particles A and B.

The quantity P is determined by the molecular dynamics of the pair and is calculated from Eqn.(23), which contains the parameters of the diffusion (p, m) and chemical (k, ϵ) dynamics. The relative proportion of the primary and secondary reactions in the pair [first and second terms in Eqn.(23)] depends on the values of the constants k and ϵ; for large k and ϵ, the proportion of the primary reaction (that is reaction at the moment of first contact of the particles) is large; for small k and ϵ, an appreciable contribution to the probability of the reaction is made by the secondary encounters of the partners in the pair. The value of P also determines the cage effect in radical reactions; the same considerations apply to the primary and secondary recombination of the radicals in the pair. The cage effect and diffusion kinetics will not be discussed here; these topics have been dealt with in a number of reviews and monographs (see for example Refs.112 and 113).

The parameter ϵ (that is the probability of reaction in a contact pair) depends on the competition of the rotational and translational mobilities of the particles. It is usually described effectively using the black spot model. It is assumed that the reacting particles are spheres with marked anisotropy of the reactivity; in other words, the reaction centre occupies only a small fraction (the "black spot") of the surface of the sphere. If contact between two such spheres is to be accompanied by reaction, it is necessary that their relative orientation lead to the coincidence of the two "black spots". This model has been examined in detail[114]; the probability of reaction depends on the ratio of the frequencies of rotation and translation and on the size of the "black spot".

The "black spot" model has been confirmed by recent data[115] The disappearance of t-butyl radicals in C_7-C_{16} hydrocarbons is a diffusion-controlled process with rate constant 10^8-10^9 litre mole^{-1} s^{-1}; the ratio of the yields of the disproportionation and recombination products (f_d/f_c) decreases with increase in temperature and decrease in the viscosity of the solvent. This dependence is explained as follows. For t-butyl radicals, disproportionation takes place in the pair for many relative orientations; in other words, the set of states from which disproportionation takes place is large, that is the "black spot" is large for disproportionation and small for recombination (the ratio of their areas is ~20). Increase in temperature and decrease in viscosity lead to an increase in the frequency of the rotations and an increase in the probability of contact of the "black spots" responsible for recombination; the probability of recombination therefore increases more rapidly than the probability of disproportionation. The ratio f_d/f_c should therefore decrease until it is determined purely by the chemical reactivity ($k_d/k_c \simeq 3$).

This dependence of f_d/f_c on temperature and viscosity, predicted by the "black spot" model, agrees with the experimental results. For reactions controlled by activation, that is taking place under kinetic conditions, molecular dynamics does not play a significant role; it may be revealed only in exceptional cases (in very viscous solutions or in reactions involving macro-molecules). For solid-phase reactions, on the other hand, even under kinetic conditions, the chemical kinetics are controlled by the molecular dynamics[116]; this is the fundamental difference between solid-phase and liquid-phase reactions.

Complex formation and solvation influence the kinetics of reactions controlled by both activation and diffusion. For reactions controlled by activation, the difference in the reactivities of the free and solvated particles is significant; the relative contributions of each to the reaction are determined by the corresponding rate constants and the solvation equilibrium constant[117]. Extensive data on the influence of solvation on the kinetics of reactions have been published[118,119]. For reactions controlled by diffusion, complex formation and diffusion influence both k_{diff} (via the translational dynamics) and P (via the reactivity and dynamics of the pair).

Thus solvation decreases the magnitude of the rate constant for the recombination of t-butoxide and peroxide radicals[119]. The diffusion coefficients of hydrocarbon molecules RH are much greater than the diffusion coefficients of the corresponding alkyl radicals R; it is suggested that this is due to solvation of the radicals[120]. The situation is particularly complicated when the solvated particles do not react, and the lifetime of the solvates is comparable with the lifetime of the pair; it is then necessary, in calculating P, to take simultaneous account of the dynamics of the pair and the dynamics of solvation.

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The dynamics of elementary processes in a liquid is part of chemical dynamics. It determines the competition of the elementary processes in pairs of reacting particles, diffusion kinetics, the efficiency of initiation in thermal, photochemical, and radiation-chemical processes, the efficiency of the utilisation and transformation of energy in chemical reactions, etc. The completeness of its description is of course still far from that for gaseous reactions (for example reactions in molecular beams), but it is being developed rapidly. The greatest contribution to the further development of this field is expected from picosecond spectroscopy.

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